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STUDIES ON THE RUBBER-FILLER INTERACTIONS IN TYRE TREAD COMPOUNDS

Master of Science thesis

Examiners: Juuli Wacker, prof. Jyrki Vuorinen and prof. Minna Kellomäki
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ABSTRACT

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Due to the low mechanical properties of pure rubber, fillers are normally added to rubber compounds intended to provide reinforcement and improve their final properties. Several factors affect the reinforcing potential of fillers, including size, structure and surface activity.

Carbon black and silica are the most common reinforcing fillers used in the rubber industry. Since the introduction of the "Green Tire Technology" in 1992 by Michelin, silica was found to offer reduced rolling resistance and enhanced wet grip properties compared to carbon black. However, silica presents many processing difficulties due to the polarity differences with rubber and requires the addition of silane coupling agents. Silane coupling agents reduces these polarity differences between silica and rubber providing strong filler-polymer linkages and thus, good final mechanical properties of rubber compounds. With the addition of silane coupling agents several reactions take place, such as the silanization reaction occurring between the silica and silane, the silane-rubber coupling and the linkages occurring between the polymer chains. All these reactions play an important role of the reinforcing potential of silica particles. Therefore, the dispersion of silica along with the filler-polymer interactions occurring within the rubber matrix are nowadays important concerns for the tyre industry. Silica particles tend to self-associate forming aggregates and lowering the mechanical properties of tyre tread compounds.

Due to the importance of rubber reinforcement in tyre industry the main aim of this thesis is to use different measuring techniques to study filler-polymer interactions occurring within the rubber matrix. The effects of compounds composition and mixing times on filler-polymer interaction were studied.

This thesis is divided into two parts: the literature review and the experimental part. The literature part consists of 5 chapters making a general overview of rubber technology, silica and silane coupling agents and the different techniques available to measure filler-polymer interactions. The experimental part contains the methods used to measure fill-

er-polymer interactions and all the results obtained from each measurement. The measuring techniques used in this thesis includes flocculation kinetics studies, cure curve studies, bound rubber tests, tensile test, Payne effect and several conventional methods.

Three series of compounds were prepared making variations to the composition and mixing extensions of the reference compound. The results from series A revealed that the addition of the accelerator along with the curatives reduces notably filler flocculation and provides improved mechanical properties of rubber compounds. In addition, the effect of silane coupling agent on filler-polymer interactions can be observed. The absence of silane clearly leads to strong filler-filler interactions and thus, poor filler dispersion within the rubber matrix. Moreover, large surface silica particles results in increased flocculation due to the stronger interparticle forces leading to the formation of agglomerates.

From series B it can be observed that increased amounts of accelerator and silane coupling agents increase the degree of filler-polymer interactions occurring when large surface area silica is used. The use of masticated rubber does not show any effect on filler-polymer interactions.

The results obtained from series C indicates that extended mixing action increases the degree of silanization and better filler dispersion is reached. On the contrary, shorter mixing time results in increased filler flocculation and worse final properties of the rubber compounds.

PREFACE

This Master's thesis was carried out in Tampere during the period June 2015-March 2016. It was for me a great privilege to have the opportunity to work in this master thesis surrounded by such good professionals. This unforgettable experience was certainly one of the most enriching in my life and for that reason I would like to thanks to all the people that supported and helped me to make it possible.

Firstly to my helpful and dedicated supervisor, Juuli Wacker, who gave me the opportunity to work for Nokian Tyres. I would like to thank her for her valuable guidance and encouragement with a kind and understanding spirit that helped me a lot with the accomplishment of this thesis.

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For all these people that makes this thesis possible THANK¡ from the bottom of my heart. It was a pleasure to share this experience with all of you.

Tampere, 14.3.2016

María del Carmen Gamero Rodríguez

CONTENTS

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LIST OF SYMBOLS AND ABBREVIATIONS

ADS	Air-dried sheet
APA	Advanced polymer analyzer
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller theory
BR	Butadiene rubber
C	Carbon
CBS	N-Cyclohexyl-2-benzothiazylsulphenamide
CIIR	Chlorobutyl rubber
CO_2	Carbon dioxide
CTAB	Cetyltrimethyl ammonium bromide
CTP	N-Cyclohexylthiophthalimide
DBP	Dibutylphthalate
DMA	Dynamic mechanical analysis
DPG	Dyphenylguanidine
DTDM	Dithiodimorpholine
E-SBR	Emulsion polymerized styrene-butadiene rubber
IIR	Butyl rubber
ISO	International organization for standardization
MDR	Moving die rheometer
NR	Natural rubber
ODR	Oscillating disc rheometer
Phr	Parts per hundred rubber
PPDs	P-phenylene
PY GC/MS	Pyrolysis gas chromatography/ mass spectrometry
RPA	Rubber process analyzer
RSS	Ribbed smoked sheet
SBR	Styrene-butadiene rubber
SiO2	Silica
S-SBR	Solution polymerized styrene-butadiene rubber
STSA	Statistical thickness surface area
TBBS	N-tert-butyl-2-benzothiazylsulphenamide
TESPD	Bis-(triethoxysilylpropyl)disulfide
TESPT	Bis-(triethoxysilylpropyl)tetrasulfide
Tg	Glass transition temperature
TMDT	Tetramethylthiuram disulfide
UV	Ultraviolet

1. INTRODUCTION

1.1 Historical overview of rubber technology

Natural rubber (NR) was firstly observed by Cristobal Columbus during his American voyage in 1493. Natives from Haiti used to extract the fluid of a tree called "caa-o-chu" (weeping tree) and condense it afterwards in order to use it as a material for their local ball game as well as for making their clothes water proof. This tree was later on named as Hevea Brasiliensis and the liquid being extracted from it is known as latex. The discovery of NR supposed the starting point of rubber technology which in 1736 was brought to the Academy of Science in Paris. Promptly, the scientists discovered the multiple applications of this material which presents unique properties. The first important application of the dried latex was as eraser of pencil marks. [1, 2]

The next important discovery in rubber history was made in 1839 by an engineer called Charles Goodyear. This skilled scientist successfully discovered that mixing rubber with sulfur under thermal conditions resulted in improved properties of rubber products. This process was named "vulcanization" after the Roman God of Fire, Vulcan and nowadays is still the key process in rubber technology. [1, 2]

The enhancement of rubber resistance within vulcanization along with its unique elastic properties immediately increased the use of this material for a wide variety of applications. Especially with the invention of automobiles the demand of rubber rapidly increased. The first developed tyre was a solid rubber sheet covered with fabric. By the end of the 19th century, André Michelin introduced the concept of air-filled tires overcoming the problem of flat tired after one decade and a half. Finally, J.B Dunlop brought the pneumatic tire to the automobiles. [1, 2]

The last great achievement in rubber technology was the replacement of carbon black by silica fillers. The first precipitated silica was introduced by the Columbian Chemical Division of the Pittsburgh Plate Glass Co. LTD in 1948. Silica reinforcing fillers lead to lower rolling resistance tyres (approx. 20%) and consequently reduced fuel consumption of the vehicle (approx. 4%) compared with carbon black. Even though the production costs of tires containing silica fillers are higher, the environmental and economic benefits make feasible the use of silica as reinforcing fillers. [1, 2]

1.2 Background and aim of the thesis

In tyre applications all tyre tread compounds are reinforced by reinforcing fillers, mostly either carbon black or silica. The reinforcement of tyres is essential in order to improve the final properties of the rubber compounds such as strength, heat resistance, abrasion resistance and tear strength. [1]

As documented in previous section, the use of silica as reinforcing filler has been extensively growing in the last decades due to its numerous advantages compared with carbon black. However, the main drawback of silica is associated to its difficult processing behavior as result of polarity differences between silica and non-polar rubbers. Silica particles present a highly hydrophilic character due to the high concentration of silanol groups on their surface, while natural rubber is highly hydrophobic. This polarity mismatching leads to strong filler-polymer interactions which results in poor filler dispersion within the rubber matrix. For that reason, coupling agents are used to increase filler-polymer interactions and achieve proper filler dispersion. [1, 2]

In order to ensure good final properties of the rubber product, filler-polymer interactions must be maximized. Several parameters influence the dispersion of silica particles within the rubber matrix as it will be reviewed in posterior sections, including silica-silica interactions, silica polymer interactions and filler mobility within the rubber. [2]

Due to the importance of rubber reinforcement in tyre industry the main aim of this thesis is to use different measuring techniques to study filler-polymer interactions occurring within the rubber matrix. The effects of compounds composition and mixing times on filler-polymer interaction will be studied. Many different methods are available to detect those filler-rubber interactions, but this thesis is only focused on some of them as it will be presented in further chapters.

This thesis was carried out for Nokian Tyres in conjunction with Tampere University of Technology.

1.3 Structure of the thesis

This thesis is divided into two parts: the literature review and the experimental part. The literature part consists of 5 chapters, starting from *Chapter 1* with the historical overview of rubber technology, a general introduction to the topic and the aim of the thesis. The following chapters are divided as follows:

Chapter 2: This chapter contains a general overview of the theory of rubber technology, including rubber compounding, rubber mixing and vulcanization.

Chapter 3: In this chapter the reinforcing fillers used in the rubber industry are described. Both carbon black and silica are reviewed, with special focus on precipitated silica. Additionally, silane coupling agents used to reduce polarity differences between

silica and rubber are presented. Finally, a comparison between carbon black and silica as reinforcing fillers is made.

Chapter 4: The reinforcement concept and bound rubber concept resulting from filler-polymer interactions are presented in this chapter in order to understand the importance of reinforcing fillers in the rubber industry. Moreover, the dynamic mechanical properties of filler reinforced rubber are discussed.

Chapter 5: This chapter is focused on different measuring techniques used for testing rubber compounds. Several conventional methods are presented in addition to different methods to assess filler-polymer interactions.

The experimental part consists of three chapters: chapters 6, 7 and 8. *Chapter 6* presents the material and experimental techniques used within this thesis, including the preparation of the rubber compounds and the methods followed within each measurement. *Chapter 7* presents the results obtained from each measuring technique used in this thesis to evaluate filler-polymer interactions. Finally, Chapter 8 contains the overall conclusions of the thesis.

2. BASICS OF RUBBER IN TYRE INDUSTRY

Rubber is defined by the ASTM standard D1566 as: “A material that is capable of recovering from large deformations quickly and forcibly, and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent. A rubber in its modified state, free of diluents, retracts within 1 minute to less than 1.5 times its original length after being stretched at room temperature (18 to 29°C) to twice its length and held for 1 minute before release”.

Rubber is an engineering material used worldwide because of its unique properties including elasticity, resilience and toughness. Rubber molecules are arranged in a long-chain and flexible form showing specific and unique behavior with properties between solid and liquid, solid appearance and capable of undergo important deformations. *Elasticity* is the most remarkable rubber property providing to rubber molecules the capacity of fast molecular movement under deformations being able to return to its original state after the applied forces are removed. [3, p. 304]

Rubber can be either natural rubber (NR) derived from extraction of certain tropical plants or synthetic rubber derived from natural gas and petroleum. [3, p. 303] The global rubber consumption in 2013 was estimated to be 26.8 million metric tons, where natural rubber counted for 11.35 million tons and synthetic rubber counted for 15.44 million tons. [4] Tyre industry is considered to be the major consumer of both natural and synthetic rubber counting for around 70% of the total rubber consumption; however, rubber is widely used in many other industrial, transportation, domestic, construction and aerospace applications. [3, p. 303; 5]

2.1 Introduction to tyre technology

A tyre is essentially an air chamber of cord-rubber composite, which supports the weight of the vehicle when inflated to a suitable pressure. [3, p. 656] Its main functionality is to transfer the actions applied by the driver, such as accelerating, turning and braking. Moreover, tyres play an important role in the suspension system of a vehicle, absorbing the shock of road roughness and providing smooth and safe ride. [4]

Tyres are made of a series of different parts from different materials, each of them having a specific function in the performance of the final product. [3, p. 656] Figure 1 illustrates the cross-section of a car tyre. The components of the tyres are presented as follows:

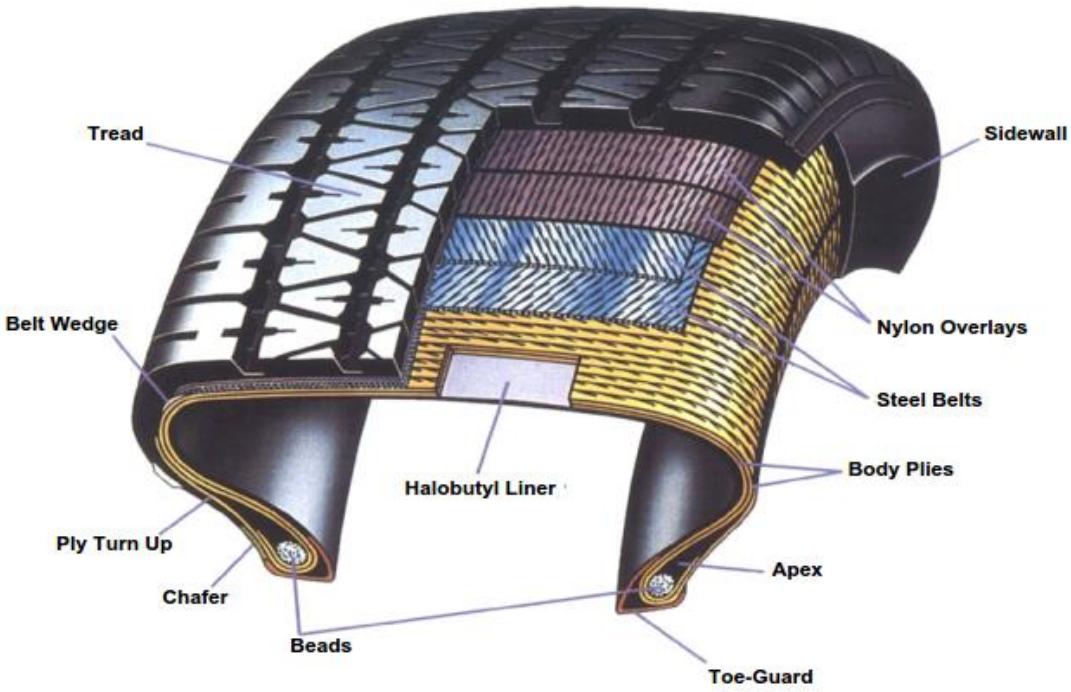

Figure 1. *Cross-section of a high performance passenger tire. [3, p. 656]*

- ***Tread:*** the tread is the most influencing component on the final tire performance. It is the largest and thickest component of the tyre, since it is in direct contact with the road. [5, p.6] In addition to provide protection to the tyre casing, its main role is to provide wear resistance. It must provide also wet grip and traction, along with low heat buildup and noise generation. [6, p.354]Tread components can be composed of a large variety of blends of natural rubber (NR), polybutadiene (BR) and styrenebutadiene rubber (SBR), mixed with carbon black, silica, oils and vulcanizing agents. [3, p. 657]
- ***Belts:*** they are located under the tread and they consists of layers of steel or textile wire layered at bias angles, which are intended to stiff the casing providing stability and damage resistance to the tyres. [4] Moreover, the belts enhance wear properties and handling response of tyres as they offer a controlled contact with the road eliminating the interfacial slippage. They also serve as protection for the carcass. [3; 5, p.6]
- ***Carcass:*** the carcass is the main body of the tyre and it is made of rubberised textile cords such as rayon, nylon, polyester or steel cords. It extends from bead to bead, thus being the main reinforcing material of the tyre casing. The primary functions of the carcass are to sustain the inflation pressure and resist load and road shocks. The shape of the carcass is determined by the cord angle and it is possible to distinct between crossply tyres (± 30° cord angle) and radial tyres (90° cord angle). [6, p.353-354]
- ***Sidewall:*** the sidewall is the thinnest and most flexible part of the tyre consisting of a protective rubber coating on the outer sides of the tyre. It is intended to provide protection to the carcass, to make the ride more comfortable by resisting

flexing and weathering and to provide assistance in tread support. [3, p. 657] Since the sidewall will be exposed to many degrading agents, it requires to be compounded with additional ingredients in order to prevent ozone or oxidative attack. [5, p.5] Additionally, it contains all the tyre markings and identification information printed on it. [4]

- ***Bead wire:*** it consists of high tensile strength steel wire loops coated with bronze and insulated with rubber, holding the tyre on rim and maintaining it in position by tyre pressure. [6, p. 354]
- ***Innerliner:*** it is the inner layer that covers the inside of the tyre from bead to bead and keeps the compressed air inside the tyre avoiding air loss. It is typically made of low permeability rubber such as butyl rubber or halogenated derivatives. [3, p. 658]
- ***Chafer:*** it is a layer of abrasion resistant rubber which protects the carcass at the bead area from the heat generated by the chafing of the bead against the rim flange. [6, p. 354]
- ***Apex:*** it consists of rubber filler in the void area of the bead and lower sidewall with triangular cross-section. Its main function is to provide gradual transition from the stiff bead area to the more flexible sidewall. Stiffness and hardness are the most important properties required for materials forming the apex, thus, providing durability and good vehicle handling. [6, p. 354-355]
- ***Cap-ply:*** they are mostly found in high performance car tyres and they consist of sinlge or multiple sheets, usually of nylon, that cover the belt completely or only the belt edges. They give extra contractive force in order to prevent the growth of the belt edges caused by centrifugal forces. [5, p.4]

The tyre manufacturing is a very complex and meticulous process which can be divided into five different steps [3, p. 688-689]:

1. Raw materials are mixed to form the rubber compound.
2. The components are prepared by using three different processes:
    - Extrusion to prepare the tread and sidewall.
    - Calendaring to prepare the belt package, the carcass and the innerliner.
    - Bead building.
3. The components of the tyre are assembled on the tyre building machine to build the so-called “green tyre”.
4. The “green tyre” is cured in a curing press under heat and pressure.
5. Inspection of the final tyre both visually and automatically is conducted in order to detect any defect on the final product.

The final product needs to fulfill many qualifications and its properties must be optimized in order to meet with the market demands. The most important properties of a tyre are presented in the following chapter.

2.1.1 Tyre properties

Tyre performance is dependent of many parameters and it has to fulfil many qualifications in order to meet with the required final product properties. There are three major indicators of tyre performance: wet traction, abrasion resistance and rolling resistance; they form the so-called "magic triangle" by tyre manufacturers. Figure 2 represents the tyre magic triangle. [7]

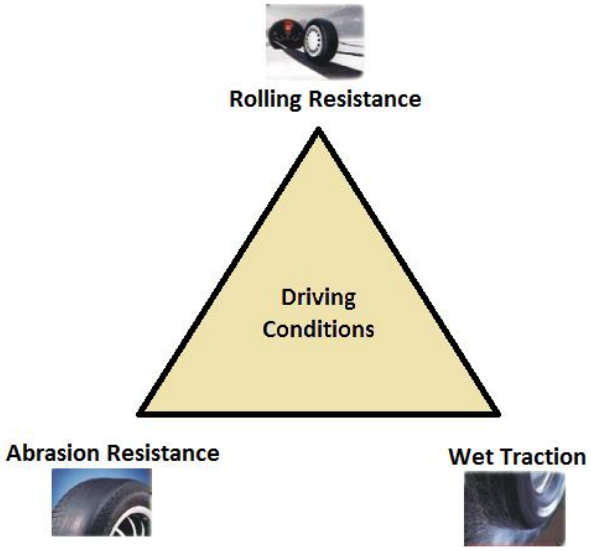

Figure 2. *Tyre magic triangle*.

These three properties are conflicting parameters since it is not possible to enhance three of them simultaneously. A balance between these properties must be achieved so that a proper tyre performance can be provided. [8]
A tyre must show high traction properties as well as cornering forces on both wet and dry roads; these are the so-called wet and dry grip. By means of this high traction force, slippage is avoided by creating a good grip on the road surface. In addition, predictable steering characteristics are required under every handling situation. Traction properties are influenced mainly by three tyre features; the construction of the tyre, compound of the tyre tread and its profile design. [7, 8]

Low wear and good durability are also required properties of a tyre. Furthermore, it must provide satisfactory driving comfort and offer high abrasion resistance to create high mileage.

On the environmental and saving point of view, the rolling resistance of a tyre must be as low as possible, thus inducing improved fuel efficiency. Rolling resistance is gaining a lot of interest on the last decades and much effort by tyre manufacturers is

intended to reduce it, while simultaneously enhancing other parameters of tyre performance. [7]
Rolling resistance plays an important role in fuel consumption: between 5 to 15 % of total fuel energy is consumed by rolling resistance on passenger cars and light trucks. The tread compounding is a determinant factor to reduce rolling resistance without affecting other aspects of tyre performance as it is possible to control hysteresis characteristics. [7]

2.2 Rubber Compounding

Rubber compounds are formed by a mixture of certain ingredients which determine their final properties and can be varied depending on their final use. The basic properties of a compound are mainly influenced by the elastomer type; however, these properties can be satisfactorily modified by the addition of certain ingredients to the compound recipe. Normally, a rubber compound formulation contains 10 or more ingredients and each of them are intended for a specific purpose as discussed below. [6, p. 167]

2.2.1 Elastomers

Elastomer is the most important component in a rubber compound and its selection will determine the basic properties of the final product. One or more elastomers can be mixed in the recipe, being natural rubber (NR), styrene butadiene rubber (SBR), polybutadiene (BR), polyisoprene and the butyl rubber the most used types worldwide. In tyre industry, the most common elastomers are NR, SBR and BR and their characteristics and properties are presented below. [9, p. 303]

- ***Natural Rubber (NR)***

Natural rubber is a material originally extracted from the latex of many different species of plants around the world; nonetheless, 99% of commercial natural rubber is extracted from the latex of the tree *Hevea brasiliensis*, original from Brazil and known as “the rubber tree”. The extracted latex is a milky and runny white colloid consisting of polyisoprene, water and small amounts of other ingredients. [12, p.14]

Normally, the majority of the natural rubber produced is plantation rubber at which the latex is extracted and coagulated in large tanks by using formic acid or acetic acid. The latex is posterior diluted with water to solid contents in the range of 12 to 18 %. The higher the amount of water, the more amount of acid is needed for coagulation. Two coagulation methods are available for natural rubber depending on how coagulum is processed: ribbed smoked sheet (RSS) is obtained by drying the coagulum by exposure to hot wood smoke and air-dried sheets (ADS) is obtained by air drying. [12, p.14]

Nowadays, the major producers of natural rubber in the world are Thailand, Indonesia, Vietnam, India and China as it is illustrated in Figure 3.

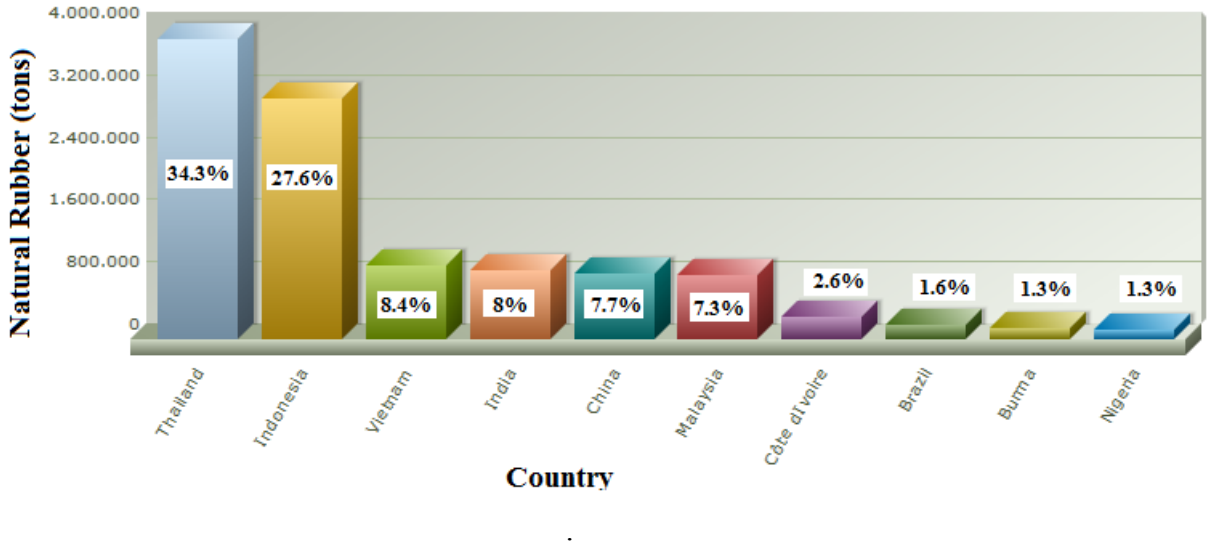

Figure 3. *World production of Natural rubber by countries in year 2013. [13]*

Natural rubber composition consists of around 99.99% of linear cis-1,4 polyisoprene as it is shown in Figure 4 and its average molecular weight ranges from 200 000 to 1 000 000 leading to excellent processing behavior. Macromolecules present in NR are long, flexible, regular and nearly linear providing extremely good elasticity properties. Glass transition temperature0 of NR is about -70 °C and spontaneously crystallizes (-25°C) under deformation forces when prolonged more than 80% due to stereoregularity. [6, p.32]

Even though the main repeating unit of NR is cis-1,4 polyisoprene, it can be classified according to its "dirt" content since the main source is a tree. The main "dirt" grades are RSS1 to RSS5 and SMR 5, 10, 20 and 50. Lower numbers mean higher grade of cleanliness and as consequence increased price. [12, p.14]

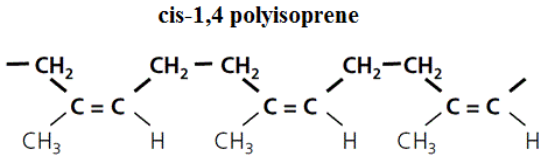

Figure 4. *Natural rubber repeating unit cis-1,4 polyisoprene.*

Natural rubber is the most widely used type of rubber in tyre industry because of its combination of favorable properties such as high strength, high elasticity, outstanding tack and green strength. Vulcanized filled NR can reach a tensile strength value of 30 MPa. [6, p.39]

- ***Butadiene Rubber (BR)***

Butadiene rubber is an important elastomer with many relevant properties; however, it is normally blended with other rubber types due to its difficult processing behavior on

rubber machinery. Normally, it is blended with non-polar elastomers such as Natural rubber. [12, p.24]

A diversity of isomers differing on the position of the intersection (1,2 or 1,4) can be produced from the polymerization of 1,3-BR. Depending on the orientation of the substituents present in the double bond, 1,4 polymerised BR is available as cis- or trans-structure as in the case of 1,2-BR. Each different isomer presents its own mechanical, physical and rheological properties. In tyre industry only elastomer isomers cis-1,4-BR and amorphous 1,2-BR are of interest and additionally, mixtures of cis- and trans-1,4-BR are also used. The structure of these isomers are illustrated in Figure 5. [6, p.56-57]

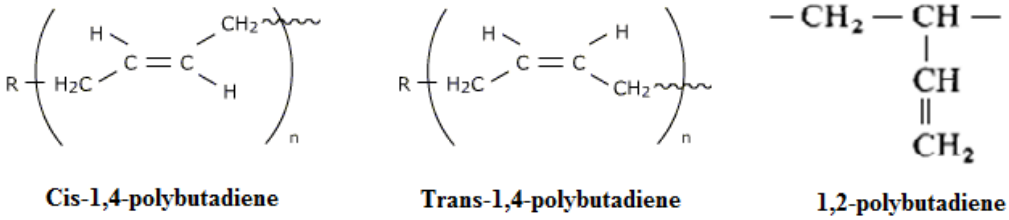

Figure 5. *Structure of different isomers of BR.*

The polymerization of amorphous 1,2-BR is made by anionic polymerization with chelating diamine modified anionic lithium alkyl producing butyl rubbers with approximately 99% of the butadiene placed at the 1,2 position. In addition, it is possible to obtain intermediate structures by controlling the temperature and the chelating modifier/anionic lithium ratio. By increasing this ratio, the vinyl content increases and so do the T_g of the butyl rubber. In tyre industry, amorphous 1,2-BR is highly used due to its low hysteresis loss and exceptional wet skid resistance properties. [6, p.56-57]

Both cis- and trans-1,4-BR are polymerized by using Ziegler-Natta catalysts. Higher cis-1,4-BR leads to lower Tg, having pure cis-1,4-BR a Tg of approximately -100°C. Normally, combinations of 96% of cis- with trans-1,4-BR are used in tyre industry due to its favorable low hysteresis along with good wear properties, providing a Tg of about -90°C. [5, p.12]

- ***Styrene-butadiene Rubber (SBR)***

Stryrene-butadiene rubber (SBR) is a styrene and butadiene copolymer containing typically 23.5% of styrene, mostly polymerized by solution polymerization (S-SBR). Solution polymerization takes place in the presence of Ziegler-Natta catalyst offering an improved control of the polymer microstructure. The use of emulsion polymerization (E-SBR) has been drastically reduced in the last decade.

The mechanical properties of both E-SBR and S-SBR are similar; however, S-SBR is broadly used in tyre industry since it presents lower heat buildup characteristics, higher resilience and consequently lower rolling resistance. Increasing styrene content leads to a higher glass transition temperature, Tg, because of the obstruction of the chain

rotation by the benzene side groups present in styrene. Therefore, it directly affects to the wet grip properties of the tyre since the material becomes less rubbery. [13] The vinyl content of the polymer also affect to the properties of the material. Increasing vinyl content increases the glass transition temperature of the rubber.

Tyre industry is the major application of SBR rubber due to its good mechanical properties, good abrasion resistance and high hysteresis.

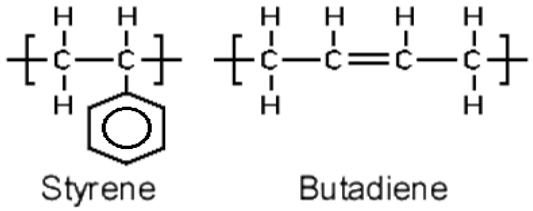

Figure 6. *Structure of SBR repeating units*.

2.2.2 Fillers

Fillers added to rubbery materials play an important role in reinforcement characteristics, processing behavior and final price of the material. Filler loading to the compound is typically 10-15 times higher than other chemicals additives and they can be either reinforcing or non-reinforcing fillers. [14, p.26]

Reinforcing fillers used in rubber industry will improve several mechanical properties of the compound such as tensile strength, hardness, modulus, abrasion resistance and tear strength. Many different types of fillers are available, but mineral fillers such as carbon black and silica are the most widely used in tyre industry. The reinforcing potential of reinforcing fillers is affected by properties such as particle size, surface area, structure and surface chemistry as it will be discussed in following chapter. [6, p.155]

Non-reinforcing fillers will be added as rubber diluents in order to reduce the price of the final product. Ground calcium carbonate is widely used as diluent due to its low price without affecting the reinforcing potential. Additionally, soft clays, barites and talc are used as non-reinforcing fillers. [6, p.155]

2.2.3 Processing aids

Plasticizers and softeners are used in rubber compounding in order to reduce the viscosity of the compound and facilitate its processing by increasing the plasticity of the material. At low levels, plasticizers help to provide proper filler dispersion. At higher levels, they help to reduce the viscosity of the uncured compound, lowering the cost, improving flexibility at low temperatures and reducing hardness. [15, p.459]

The main sources of plasticizers are petroleum oils, which can fall into three different categories: aromatic, paraffinic and naphthenic. It is thought that aromatic oils

provides better tensile strength and crack growth resistance, while paraffinic oils provide better resilience and lower hysteresis. [12, p.40-41]

In rubber industry, the most widely used plasticizers are esters, pine tars and low-molecular-weight polyethylene. The main factor determining the compatibility between rubber matrix and plasticizers is polarity. Normally, polar rubbers are compatible with polar plasticizers. [16, p.459-460]

Pine tars are very compatible with natural rubber providing good filler dispersion and improving compound properties such as adhesion and fatigue resistance, which play an important role in prolonging tyres lifetime. Other important types of plasticizers include vegetable oils, fatty acid salts, rosin and organosilanes. [16, p.459-460]

2.2.4 Vulcanizing agents

During vulcanization, chemical crosslinks between polymers chains are created determining the final rubber properties. The selection of the curing system is based on the chemical reactivity of the polymer, the stability and the crosslink type that provides better performance to the final product. Elemental sulfur is the most widely used vulcanizing agent, but peroxides and metal oxides are used as well. [9, p.308]

- ***Sulfur-based curing system***

Sulfur-based curing system is basically used for unsaturated elastomers. This type of curing system is the most frequently used in rubber industry because of its numerous advantages, including low cost, low toxicity and great flexibility. [9, p.308]

Sulfur-based curing systems consist of several components including:

I. ***Activators***. They are used to activate the accelerator and improve its efficiency. Zinc oxide and stearic acid are the most common activators, while other oxides of cadmium and fatty acid are used as well. Activators are usually required in sulfur curing systems to obtain a good crosslinking. [15, p.21]

II. ***Elemental sulfur or a sulfur donor***. Even though several sulfur grades are available, the most common form of sulfur used in this type of curing system is rhombic sulfur (S_8), an eight sulfur atoms ring soluble in rubber. Sulfur is responsible for creating the crosslinks between polymer chains. [15, p.20-21] An example of a sulfur curing reaction is presented in Figure 7.

III. ***Accelerators***. These components are used to reduce the vulcanization rate by speeding up the reaction since this process can take a relative long time. Many different types of accelerators are available and they fall into five different categories: sulfenamides, thiazoles, guanidine, dithiocarbamates and thiurams. Sulfenamides such as Cyclohexylbenzothiazole sulfonamide (CBS) or tert-Butyl-2-benzothiazole sulfonamide (TBBS) are the most used accelerator types acting as delayed accelerators. Accelerators, such as (DTDM) are able to act as sulfur do-

nors providing sulfur from their chemical structure and thus, reducing the amount of sulfur required for vulcanization. [12, p.33-34]

IV. ***Retarders and inhibitors***. Retarders are used to reduce the vulcanization rate and inhibitors to delay the starting point of the curing reaction. The most common retarded used is *N*-Cyclohexylthiophthalimide (CTP) interfering with the activity of the accelerator. [15, p.22-23]

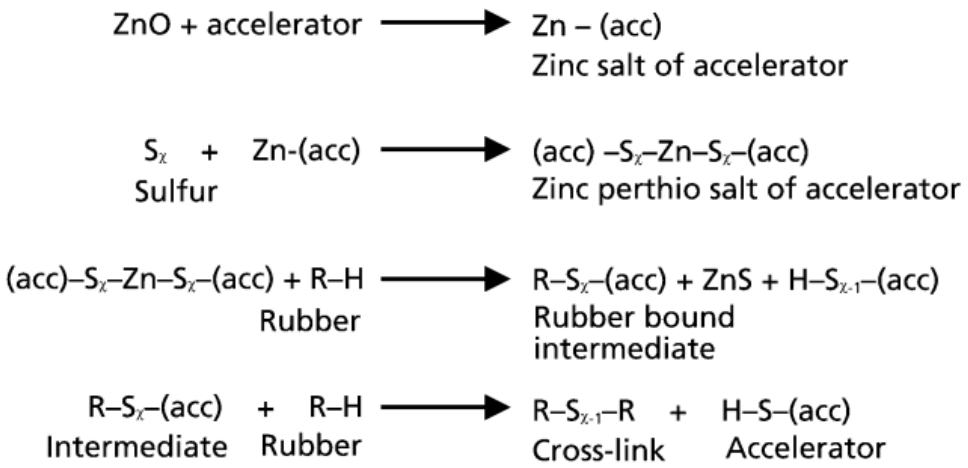

Figure 7. *Sulfur-based vulcanization reaction of diene rubbers. [9, p.309]*

- ***Peroxides***

Peroxides can be used for crosslinking most rubber types except IIR or CIIR. However, they are mostly used with unsaturated elastomers as well as with elastomers that present chemically saturated backbones and thus, sulfur vulcanization is not effective. Peroxides are the main curatives for silicone rubber. [15, p.25; 5, p.35] Some of the most used peroxides are dicumyl peroxide, zinc peroxide, benzoyl peroxide, 2,4-chlorobenzoyl peroxide and 2,5-bis(t-butylperoxy)-2,5-dimethylhexane. [6, p.170]

Within peroxide curing system the crosslinking reaction is based on thermal decomposition of peroxides into oxy radicals. Polymer radicals are formed right after these oxy radicals directly react with hydrogen of the polymer chain being able to form C-C crosslinks. The crosslinking rate directly depends on the decomposition rate of peroxide, hence, on peroxide stability. [15, p.25] During peroxide curing the ingredients required in sulfur curing are no longer needed in the curing system and peroxide is the unique effective ingredient. However, in order to increase the efficiency of the peroxides, *co-agents* such as acrylates or cyanurates are frequently used suppressing any undesirable side reaction. [9, p.310]

Crosslinks formed during peroxide curing are usually more stable than those formed by sulfur curing, providing improved heat aging resistance as well as improved compression set. Nevertheless, peroxide curing systems provide vulcanizates with reduced tensile strength, tear strength and fatigue. Commonly a post cure of vulcanizates is required in some cases so that to remove undesirable byproducts and complete curing. [15, p.25; 12, p.35-36]

- ***Metal oxides***

Metal oxides are limited normally for halogenated rubbers such as chloro- and bromobutyl rubber, polychloroprene, chlorosulfonated polyethylene and carboxylated nitrile rubbers. Usually zinc oxide is the most common metal oxide used for crosslinking. In metal oxide curing systems, the metal oxide can be used either alone or in combination with accelerators. The crosslink reaction is based on the formation of oxygen crosslinks plus the metal chloride salt when the metal oxide abstracts the allylic halogen from the neighboring polymer chain. [9, p.309; 15, p.25-26]

2.2.5 Antidegradants

Elastomers, as other organic materials, are exposed to degradation by several factors including oxygen attack, ozone attack and ultraviolet light attack. In order to avoid polymer ageing and extend its lifetime, certain antidegradants such as antioxidants and antiozonants are added to the compound. [16, p.446]

- ***Antioxidants***

Even though unsaturated polymers are more likely to oxide, most types of elastomers are subjected to oxidation. Oxidation is a cyclic free radical chain process involving chain scission and/or radical-induced crosslinking. Chain scission causes softening and weakening while radical-induced crosslinking causes hardening and embrittlement. [15, p.46; 12, p.36-37]

Primary antioxidants can be classified as secondary amines and substituted phenols and they collect the free radicals prior to their reaction with the elastomer chain. Aromatic amines, especially P-phenylene diamines (PPDs) are the largely used and most effective antioxidant type. Phenolic antioxidants are normally used with compounds where amines are no longer effective and hindered bisphenols are the most common ones. Secondary antioxidants include alkyl and alkylaryl phosphites which act destroying the hydroperoxides prior to their decomposition into radicals during storage and manufacture. [15, p.46]

Normally, antioxidants present additional protective properties such as UV-light protection, flex fatigue protection and inhibition of heavy-metal catalysis. [9, p. 310]

- ***Antiozonants***

Highly unsaturated elastomers like natural rubber or styrene butadiene rubber are specially exposed to ozone degradation. Ozone attacks the double bonds of elastomers producing their cleavage, what under strain leads to crack formation and propagation to its ultimate failure. Instead, low saturated or deactivated double bond rubbers are moderately affected by ozone attack and saturated rubbers are not affected at all. [15, p.47]

Antiozonants are available to provide both static and dynamic ozone resistance depending on the final use of the rubber compound. For static ozone resistance, the most effective antiozonants are petroleum based waxes such as paraffin and/or microcrystalline waxes. These petroleum waxes act creating a physical barrier on the rubber surface resistant to ozone attack. For dynamic ozone resistance, substituted PPDs are normally used creating an ozone reactive protective layer at the rubber surface. In tyre industry, a combination of waxes and PPDs is commonly used. [15, p.47]

2.2.6 Special purpose additives

Depending on the intended application of the rubber compound, a wide range of chemicals with special functions can be added to confer them the desired final properties. These special ingredients having specific functions include: flame retardants, colorants, dispersing agents, odorants, bonding agents, antistatic agents, abrasives and blowing agents. [9, p. 314-315; 15, p.47]

2.2.7 Rubber formulation

A rubber formulation involves a list with all the ingredients of the compound and their quantities relative to the amount of elastomer. Normally, in a recipe the amount of each ingredient is expressed as parts per hundred parts of rubber (phr), where the amount of elastomer is taken as 100 parts. Each particular compound has its own recipe. [9, p.306] Table 1 present the ingredients and amounts ranges commonly used in rubber formulation.

Table 1. *Typical ingredients and quantities of rubber formulation. [9, p.307]*

Ingredient	**phr**
Polymer	100
Curing system	5-15
Antidegradants	0-7
Coupling agents	0-2
Oils/plasticizers	0-250
Fillers	20-400
Special additives	
Process aids	0-20
Peptisers	0-3
Mill release	0-10
Flame retardants	0-300
Smoke suppressants	0-20
Tacktifiers	0-30
Pigments and dyes	0-20
Bonding agents	0-6
Antistatic agents	0-4
Odourants	0-2
Blowing agents	0-20

2.3 Rubber mixing

Mixing is considered a determinant process in rubber industry with the purpose of reaching a homogeneous distribution of additives. It involves several important processes, including incorporation, plasticization and dispersion. Rubber compounds are formed of many different components which differ in structure, viscosity and rheological behavior, making mixing a highly complicated process. [1, 17]

Intended to reduce the viscosity and homogenize the compound three different mechanisms take place to ensure a proper mixing as listed below:

- ***Laminar mixing:*** rubber compounds are mixed in a laminar flow and the predominant mechanism consists of the deformation of the high viscous matrix. Mixing occurs at low shear or elongation rates in the channels between the rotor shaft and the wall of the mixer. [18]
- ***Distributive mixing:*** the different components or properties are distributed homogeneously within the rubber matrix by different rearrangement processes. This process is dominant during the incorporation of additives and during the distribution of non-agglomerated fillers. Distributive mixing is restricted by small particles size of fillers and other molecules and at a relatively long period of time a homogeneous distribution can be theoretically achieved. [1, 18]

- ***Dispersive mixing:*** during dispersive mixing, breakdown of solid particles into small aggregates takes place under large forces. In order to break down solid particles it is required a stress level higher than the cohesive forces existing between agglomerates. This process is the most important part during mixing since the final material properties highly depends on the components dispersion. In order to get the best final properties of the rubber compound, an optimal particle size should be achieved. [1, 18]

Normally, the mixing process involves four different stages: incorporation, plasticization, dispersion and distribution. Prior to incorporation stage, the agglomerates are subdivided into smaller particles size suitable for being incorporated to the rubber. Figure 9 illustrates the different steps involved in the mixing process.

1. Incorporation

This is the first step of the mixing process and it is based on the incorporation of the subdivided components and mixing all together to form a compact mass. This is an essential step in the mixing program; otherwise the particles will not have energy enough for starting the mixing process.

2. Mastication and plasticization

Two steps of mastication and plasticization are involved in the whole mixing process so that to reduce the viscosity and change the rheological properties of the rubber compound. The principle of this step is based on the breakdown of the polymer chains turning them into an easily deformable viscoelastic state. Plasticizers are commonly added to facilitate the breakdown of the elastomer chains. [15, p.49; 1] Figure 8 illustrates how the viscosity changes during the mixing process.

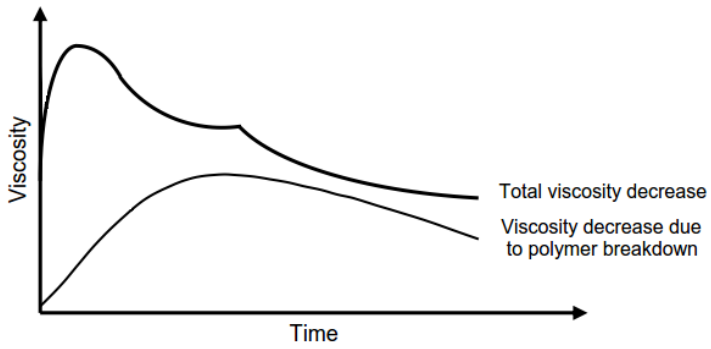

Figure 8. *Viscosity change during mixing process. [1, modified 8/2015 by M.Carmen Gamero]*

3. Dispersion

The filler agglomerates present within the rubber compound act as large and rigid particles with a large concentration of occluded rubber between the filler voids. Dispersion consists of the breakdown of the agglomerates to their ultimate aggregate size by shear stress. This reduced particles size leads to a reduction of the occluded rubber and to a homogeneous distribution of filler particles, thus, increasing the surface contact with rubber matrix. Moreover, the viscosity of the rubber compound is decreased reaching a plateau region. [1, 19]

4. Distribution

Distributive mixing consists of a homogeneous distribution of the filler particles within the rubber matrix with no particle size change involved, increasing the filler aggregates randomization. The basic principle of distributive mixing is the entropy increment of the blend. [1]

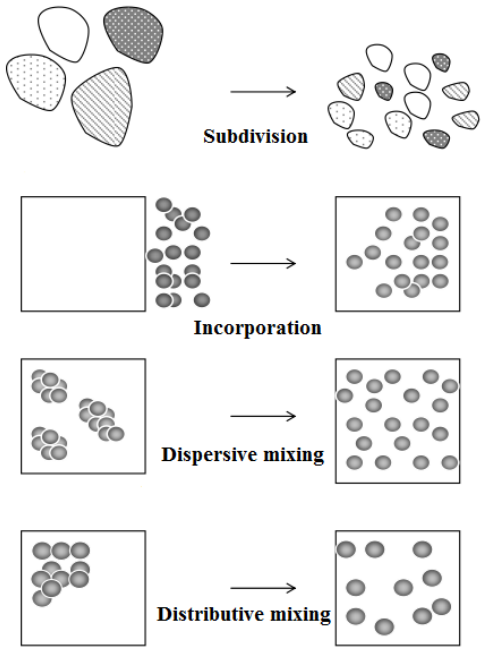

Figure 9. *Main stages of the mixing process. [2]*

Generally, rubber compounds are mixed in internal mixers in two or more steps. Firstly, the rubber, fillers, plasticizers and other chemicals are added and the curing additives are added in the final step. The initial step is mixed at high rotor speeds leading to increased temperatures, which facilitates the filler dispersion and thus, the mixing time is reduced. The last step occurs at lower temperature in order to avoid scorching since fillers are already dispersed into the rubber matrix and high temperature is no longer required. [1, 20]

A number of factors are accurately controlled since they directly affect the final mixing result, including: fill factor in percentage, ram pressure, rotor speed, dumping, air injection and geometrical design of mixing chamber and rotors. [1, 2]

Basically, two types of internal mixers are frequently available in rubber mixing differing in the shape of the rotors: *tangential mixer* and *intermeshing mixer*, which are illustrated in Figure 10. Tangential mixers have been used for a long time in tyre industry; however, nowadays intermeshing mixers are becoming more important because they provide a more accurate temperature control. [1, 2]

Tangential mixers are characterized by the flow of the compound from the sides of the mixing chamber to the center, where the shear mixing occurs. There is a gap between the rotors adjustable in some cases. Additionally, it is possible to control the speed of each rotor independently and usually one rotor works at a 10% higher speed than the other. Currently, the so-called "even speed mixing" allows an efficient mixing by working with two rotors running at the same speed and the gap adjusted at the optimum distance. The main advantages of tangential mixers include shorter mixing cycles, higher machine efficiency, and faster feeding and incorporation of the material.
Several types and profiles of tangential rotors are available all affecting in different manners to the mixing efficiency. Tangential mixers are no longer efficient in a fully filled mixer being necessary a certain empty volume, commonly the optimal fill factor ranging from 60% to 70%. [1, 20]

Intermeshing mixers are characterized by overlapping rotor tips so that the gap between rotors is fixed and both rotors work at the same speed. The most efficient mixing within this type of rotors takes place in the gap between the rotors reaching a high level of deagglomeration. Intermeshing rotors are bigger than tangential rotors so that a greater space of the chamber is occupied being the filling factor 5% to 10% smaller than that of tangential rotors. Intermeshing mixers offer more efficient cooling system and more accurate temperature control. These rotor systems are specially used when mixing silica filled compounds and present a higher mixing efficiency than tangential rotors as well as increased energy consumption. [1, 20]

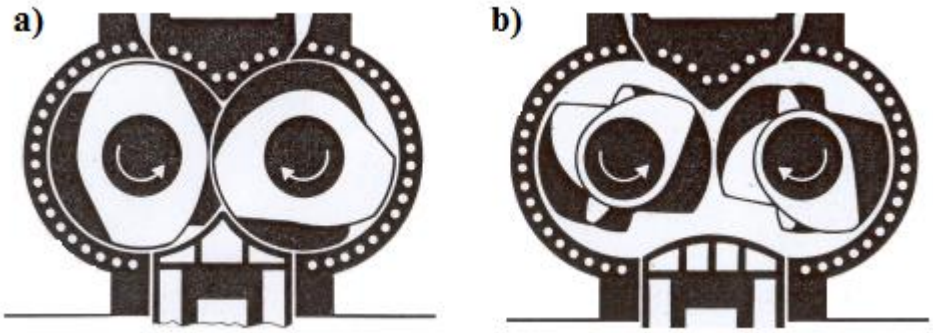

Figure 10. *Intermeshing rotor (a) and tangential rotor (b) schemes. [1, modified 8/2015 by M.Carmen Gamero]*

2.4 Vulcanization

Vulcanization consists of crosslinking reactions leading to three-dimensional network of chemically bonded polymer chains. It takes place after the rubber compound has been formed and processed changing significantly the final properties of the rubber part. [12, p.106] The overall elasticity of the rubber product is strongly increased after vulcanization process since the polymer chains interact with each other; however, the plasticity of the rubber product notably decreases after vulcanization. Crosslinks could be a single sulfur atom, a group of sulfur atoms in a short chain, a carbon-carbon bond, a polyvalent organic radical or metal ion, or an ionic cluster. [16, p.338] An example of the structure of an elastomer before and after sulfur vulcanization is presented in Figure 11. Cured rubber is a dimensionally stable and heat resistant material with enhanced final properties. [12, p.106]

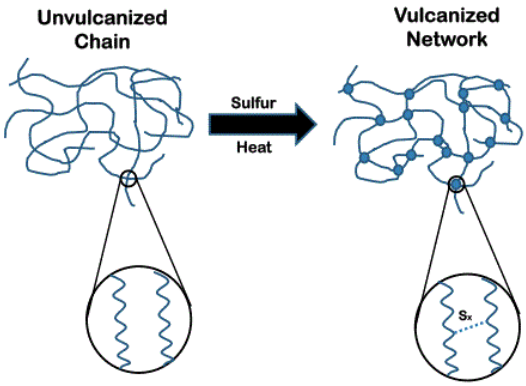

Figure 11. *Sulfur vulcanization. [21]*

Usually, vulcanization process is divided into three stages: induction, curing and reversion or overcuring. These crosslinking reactions can be monitored with a rheometer providing curing curves as illustrated in Figure 12. Values of t10 and t90 refer to the

time at which 10% and 90% of the maximum torque is reached and the difference between these values indicates the curing time. The maximum value of torque reached within the curing curve indicates the mechanical properties of the rubber.

During the induction stage crosslinks are still not formed and the safety margins to avoid "scorch" are determined. Scorch is undesirable premature crosslinks formation caused by heat and time resulting in unusable and disposable batches. Scorch time is determined by the processing and additives employed. [15, p.51]

The curing time refers to the appropriate amount of time required for the compound to reach the desired final properties and it is partly determined by the "rate of cure", i.e. the rate of crosslinks formation. [15, p.51]

A compound is overcured when it is cured to a point where the properties are no longer optimized and the rubber compound becomes harder, weaker and loses elasticity. Especially with natural rubber, the rubber compound becomes softer, less elastic and more plastic resulting in reversion. [15, p.51]

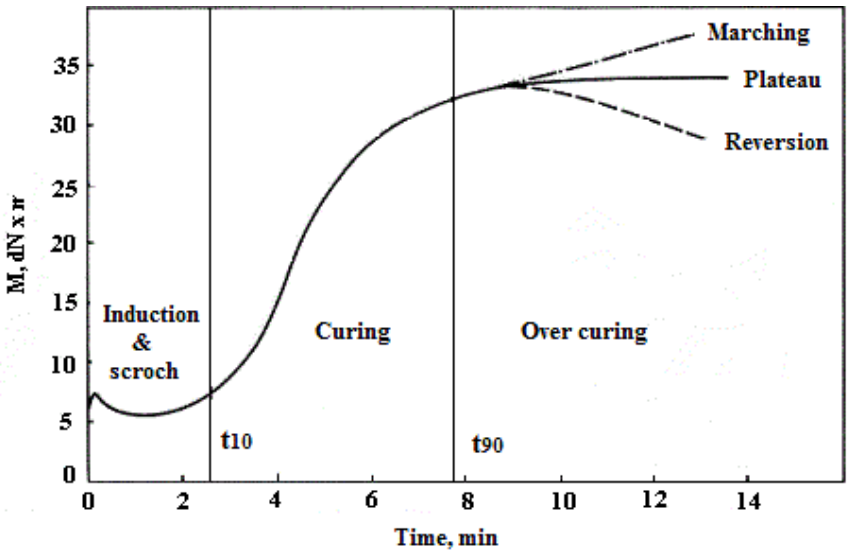

Figure 12. *Curing curve of elastomers. [22]*

After vulcanization, polymer chains are linked together producing important changes at molecular level, ranging the distance between crosslinks from 4000 to 10000 daltons. Vulcanizates become insoluble to solvents so that vulcanization needs to be accomplished when the rubber part is in its final form in order to avoid posterior processing problems. Figure 13 presents the effects of vulcanization on the final rubber properties. As it can be observed, the static modulus increases at higher rate than dynamic modulus during vulcanization. Static modulus refers to the elastic component of the rheological behavior, while dynamic component refers to the viscoelastic behavior. Additionally, it can be noticed that hysteresis ratio is reduced during vulcanization and properties like tear strength, fatigue life and toughness increase to an optimum value and subsequently decrease as well as strength properties. [16, p.339-340]

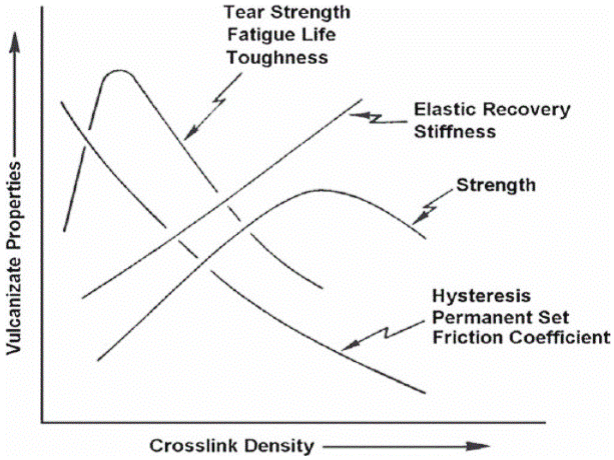

Figure 13. *Effect of vulcanization on rubber properties. [17, p.339]*

3. REINFORCING FILLERS IN RUBBER INDUSTRY

3.1 Classification of fillers

Fillers in rubber industry can be classified according to different properties: reinforcement, color, source and shape. Reinforcement concept refers to the improvement in the tensile strength, tear strength and abrasion resistance of the filled rubber. These mechanical properties are extremely important in tyre industry in order to evaluate the performance of the tread tyre compound. [23] Based on their reinforcing capability and as it is shown in Figure 14, fillers can be divided into three categories [9, 23, 24]:

- **Non-reinforcing fillers:** particles larger than 10^3 nm do not have ability to reinforce rubber materials and normally result of an increment in the viscosity of the compound. They only act as diluents so that to reduce the production costs.
- **Semi-reinforcing fillers:** semi-reinforcing fillers range from 10^2 to 10^3 nm and they are able to improve strength and modulus properties.
- **Reinforcing fillers:** reinforcement is obtained with particles smaller than 10^2 nm and the three mechanical properties mentioned above are enhanced with this particle size.

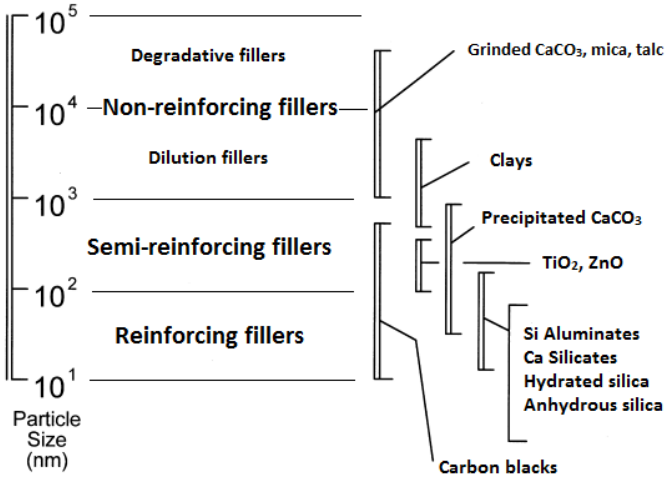

Figure 14. *Classification of fillers according to their reinforcing capability. [24, modified 7/2015 by M.C. Gamero]*

Specially, two types of minerals have been found to show important reinforcement potential: S*ilica and Carbon black*. These two reinforcing fillers are the most widely used in the rubber industry and they will be studied in the following chapter.

3.2 Filler properties influencing rubber reinforcement

There are several filler characteristics having great influence on the final rubber compound properties, including particle size, surface activity, surface area and structure. [16, p.26]

Particle Size – The particle size of the fillers will determine the effective contact area between the filler and the polymer matrix. [25] In order to avoid areas of localized stress leading to rupture of polymer chains, the filler particle size should not surpass the distance between polymer interchain. Fillers particles sizes exceeding 10^4 nm must be avoided since they reduce the compound performance. [16, p.27] Nevertheless, reinforcing fillers (10-10^2 nm) notably enhance the properties of the rubber giving increased Mooney viscosity, tensile strength, abrasion resistance, hysteresis and tear resistance as well as lower resilience. [26, p.227]

Surface Area – Fillers with larger surface areas possess higher contact area available to be intimately linked with rubber chains, thus, increasing the reinforcement potential of rubber matrix. The particle shape also influences the surface area available. Planar shape particles have higher surface contact area than spherical particles when referring to particles with the same average diameter. [16, p.27]

Structure – The structure or anisometry of the filler particles greatly influences the restriction in mobility of the polymer chains under strain. [6] Normally, fillers used in rubber industry present round primary particles shapes functioning as anisometric acicular aggregates whose properties (i.e. shape, density and size) are determinant to define their structure. In order to reach proper reinforcing potential high structure particles are required, meaning large particle size and aggregates deviating from solid spherical shape. [16, p.28]

Surface Activity – Surface activity is the determinant factor in filler-polymer and filler-filler interactions. [6] The surface activity of fillers per cm^2 of filler-elastomer interface depends on their chemical and physical nature and their compatibility with the elastomer. In the case of non-polar rubbers, non-polar fillers are the most compatible ones, however, for polar rubbers polar fillers are the most suitable. This chemical compatibility is the driving force that induces reaction between the elastomer and the active sites on filler surface. Normally, black fillers offer increased surface activity and affinity to the most common rubber types. [16, p.29]

3.3 Carbon black as reinforcing filler

Carbon black is the most used reinforcing filler for polymers, particularly in rubber industry for tyre applications. [9, p. 78] Basically, carbon black consists of extremely fine amorphous particles of elemental carbon owing its reinforcing potential to its surface properties and its colloidal morphology.

There are two basic methods to produce carbon black, *incomplete combustion of hydrocarbons* and *thermal cracking*. Based on their production process, carbon blacks can be classified as furnace blacks, channel blacks, thermal blacks and lamp black, accounting for over 95 % carbon black produced by furnace process. [27, p. 13,14] Table 2 presents the specifications of different type of carbon black based on their production processes.

During the furnace process, the preheated aromatic oil feedstocks are heated at temperatures ranging from 1400 and 1800 °C in a tubular reactor, where they are combusted and decomposed. At higher temperatures of the flame it is possible to obtain finer particles due to a higher combustion ratio. After that, the reaction is cooled down by sprayed water preventing any secondary reaction. In the final stage, the soot is collected through bag filters and subsequently pulverized and pelletized. The characteristics of the final product will vary according to the reaction parameters employed. The final product consists of around 97 to 99 % of elemental carbon, while the remaining 1 to 3 % is hydrogen, sulfur, nitrogen and oxygen. This chemical composition influences the final morphology and surface chemistry of the carbon black particles. [28]

Table 2. *Specifications of different carbon blacks based on their production process. [28]*

Characteristics	**Lamp**	**Channel**	**Furnace**	**Thermal**
Average particle size (nm)	100-150	1-3	14-80	240-320
Surface area (N_2) (m^2/g)	20-95	100-1125	27-145	7-11
Oil absorption (ml/g)	1.05-1.65	1.0-6.0	0.67-1.55	0.32-0.47
Volatile matter (%)	0.4-0.9	3.5-16.0	0.3-2.8	0.1-1.0
Ash (%)	0-0.16	0-0.1	0.1-1.0	0.2-0.5
Sulfur (ppm)	-	0-0.1	0.5-1.5	10
pH	3-7	3-6	5.0-9.5	7-9

3.3.1 Carbon black characterization

Carbon black is characterized according to its structure, surface area and surface activity as follows.

Surface area

The surface area of carbon blacks determines the contact area available to create attachments with rubber chains and it is directly determined by the particle size and distribution. [30, p.289] Normally, furnace carbon black particles are submicrometer in size (from 10 to 300 nm) and their surface area ranges from 5-150 m^2/g. Surface area or primary particle size is usually determined by different adsorption methods, including [2, p. 80]:

a) *Iodine number*. The iodine number is expressed in milligrams of iodine absorbed per gram ($mg.g^{-1}$) of carbon black. This method can be misleading since carbon black is highly porous [27, p. 14]
b) *Cetyltrimethyl ammonium bromide (CTAB*). It is based on the adsorption of large CTAB molecules and the external surface area accessible by elastomers is analyzed. This method is commonly used providing more reliable results. [25]
c) *BET method*. In this method, liquid nitrogen is adsorbed onto the carbon black surface, providing information about total surface area including porosity.[25]
d) *Statistical Thickness Surface Area (STSA)*. This method has increased hugely its use giving also values of the external surface area of carbon blacks as with CTAB method. [25]

Generally, smaller particles size have increased surface area and increased cost but higher reinforcement potential. [30, p.289]

Structure

Structure of carbon blacks plays an essential role in determining the final properties of the rubber compounds. [9] It refers to the degree of irregularity of carbon black particles and its development of branches to form aggregates. It is common to differentiate between primary and secondary structures of carbon black. [30, p. 289] Figure 15 presents an illustration of these two possible structures.

Primary structures consist of primary particles that fuse together to form three dimensional aggregates. High structure carbon blacks present strong aggregation containing a high number of primary particles per aggregate, while low structure carbon blacks present weak aggregation. Primary structures require great amount of energy to undergo breakdown during mixing and dispersion. [24, 11]

Secondary structures make reference to the agglomeration of a number of these aggregates by Van der Waals attractive forces and/or polymer bridges. During mixing and dispersion these secondary structures are easily and irreversibly disrupted. It is pos-

sible that the disrupted agglomerates reversibly fuse together again, and this is the well-known phenomenon so-called flocculation. [31]

The structure is normally measured by two different methods – evaluation of the absorption of liquid dibutylphthalate (DBP) or assessment of specific volume under mechanical compression. Both measurements are based on the evaluation of the amount of empty spaces between the fused carbon particles in the aggregate. [24]

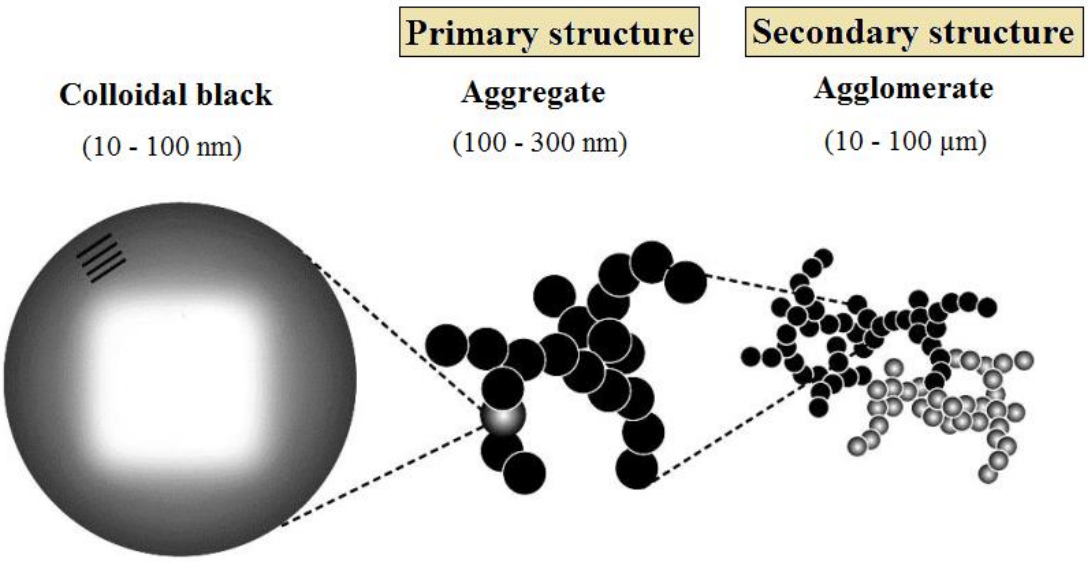

Figure 15. *Basic forms of carbon black. [32, modified 7/2015 by M.C. Gamero]*

Surface Activity

Surface activity refers to the surface chemistry of carbon black, i.e. the reactivity of the chemical groups associated with particles surface. The amount of high energetic sites on the particles surface is a key parameter determining the reinforcing character of carbon black. The main primary chemical groups present on the surface are oxygen complexes such as carboxyl, phenol, carbonyl, hydroxyl, ethers, quinones and lactones, as it can be observed in Figure 16. [24] It is thought that due to the presence of these reactive chemical groups and because of the irregularity of crystalline planes, carbon black is able to form such strong interactions with polymer molecules. Carbon blacks are considered to have a very active surface and its interaction with polymer chains is physical in nature (physisorption). [24] Bound rubber formation is a clear example of their high reactivity, referring to the mechanical locking of polymer chains onto the filler surface. [9, p. 80]

The surface activity of carbon black can be modified by heat treatment at temperatures of 1500-2700 °C strongly influencing the final properties of the rubber compounds. This modification results in a decreased bound rubber formation, reducing the high strain modulus, abrasion resistance and tensile strength. The reason may be attributed to an ordered arrangement of primary particles at increased temperatures lead-

ing to significant changes on their microstructure and thus, decreasing the high-energy sites. Based on that, it can be assumed that the origin of surface activity depend on the disordered arrangement of crystals on particles surface. [9, p. 80; 3]

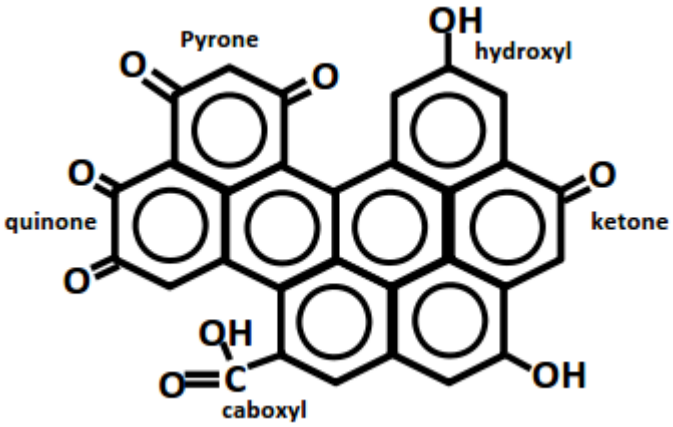

Figure 16. *Surface chemistry of carbon black. [21]*

3.4 Silica as reinforcing filler

Nowadays, several forms of silica (SiO_2) are commercially available for different industrial applications, including natural and synthetic varieties. Two types of synthetic silica based on their manufacturing methods are currently used in elastomer technology; these are precipitated silica and fumed silica. Precipitated silica finds it major application in tyre industry for rubber reinforcement. [9, p. 81] It is produced by acidification of sodium silicate solution with sulfuric acid or a mixture of HCl and CO_2 under controlled conditions. The product of this acidification is passed by a filter press, washed, dried and de-agglomerate, leading to the formation of clusters by coagulation of primary particles. Morphological features of the obtained precipitated silica are comparable to those of carbon black. Precipitated silica presents great reinforcing potential providing rubber compounds with enhanced tensile strength, tear resistance, hardness and abrasion resistance. Its characterization is based on specific surface area and particle size. [27, p. 15]

3.4.1 Silica characterization

Silica is characterized according to its particles size and distribution, its structure and it surface chemistry.

Surface area

Primary particles of precipitated silica normally range from 10 to 100 nm and its specific surface area is usually determined by two different techniques: *BET* and *CTAB* methods. [2; 33, p.170]
BET method provides measurements of the total surface area of the particles including pores, thus, magnifying the accessible surface area. Normal BET values ranges from 50 to 350 m^2/g. [2]

CTAB is the most common method used to determine the surface area of silica particles since CTAB molecules are not able to penetrate the pores due to their larger size, and thus giving more accurate values of the external surface area of particles. Typical values of CTAB methods range from 100 – 200 m^2/g. [2; 15, p.170]

High surface area of silica leads to better filler dispersion in the rubber matrix, however, it affects negatively to its processing behavior since it causes an increment in the compound viscosity. [1]

Structure

The structure of silica is a very important parameter highly influencing its reinforcing character. Precipitated silica is amorphous, consisting of very small particles that fuse together forming larger structures called aggregates. Aggregates can contain several hundreds of primary particles and are assumed the effective units reinforcing rubber compounds. Many different particle arrangements can be reached with the formation of aggregates, strongly affecting the physical properties and performance of silica. [9, p. 82]

Structure of silica is normally measured by adsorption of dibutylphthalate, known as DBP method. This method provides values of 175 g/ 100 g for conventional silicas and 200 g/ 100 g for highly dispersible silicas. [2]

Surface chemistry

The composition of silica surface is based on siloxane and silanol groups. The content of silanol groups on silica surface in addition to the degree of hydration, the amount of adsorbed water and the acidity are the key parameters influencing the surface properties of silica, such as rheology, viscosity, thickening and absorption. [33, p. 170]

There are three categories of hydroxyl groups present on the surface of silica as it is showed in Figure 17: *isolated* (single silanol) silanol groups, *vicinal* (two silanols on adjacent silicon atoms) silanols and *geminal* (two silanols on the same silicon atom) silanols. The formation of these different types of silanol groups depend on the precipitation conditions. [33, p. 170] The silanol groups present on the surface tend to interact with each other by hydrogen bonds forming strong agglomerates. These groups are also able to react with other chemical compounds reducing the availability of free silanols

that interact with coupling agents, thus, reducing the efficiency of the silanization reaction. [1]

Silica contains a strong hydrophilic character which induces the absorption of water into the surface affecting negatively to the final properties of the product. Nevertheless, certain amount of moisture is necessary for the silanization reaction to take place. [1]

The amount of silanol groups on the silica surface directly influences the average size of silica aggregates. Increased aggregate size is obtained when higher amounts of silanol groups are present, therefore, greater formation of occluded rubber. [1]

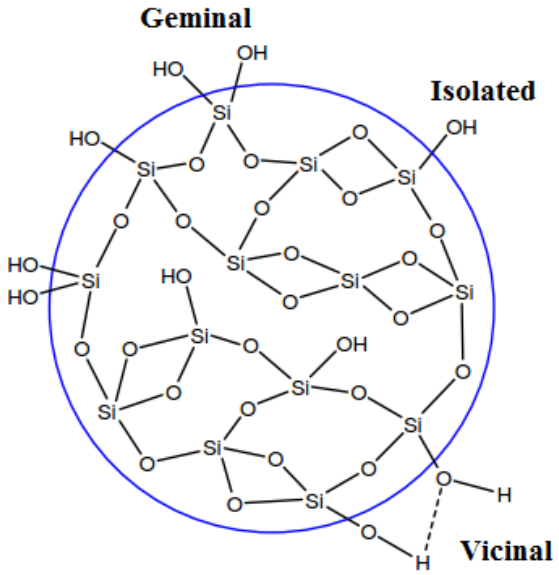

Figure 17. *Silanol groups present on silica surface: Geminal, Isolated and Vicinal. [28, modified 7/2015 by M.C. Gamero]*

Surface energy

The energy on silica surface is distributed irregularly because of the distribution of the siloxane and silanol groups as well as the impurities. The surface energy (γ_s) of silica can be described as follows [1, 2]:

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \quad (1)$$

Where γ_s^d is the dispersive component and γ_s^{sp} is the specific component.
The dispersive component refers to the rubber-filler interactions and is affected by the extent of hydration of silica; at higher water content the dispersive component is reduced. Normally, the dispersive component of silica is fairly low resulting in small reinforcing capacity leading to reduced bound rubber formation and low modulus at large and medium amplitudes. Nevertheless, certain amount of rubber is trapped between the

voids of agglomerates and aggregates and this refers to the so-called *occluded rubber*. [1, 2]

The specific component refers to the filler-filler interactions by means of hydrogen bonds, dipole-dipole forces and induced dipole forces. In the case of silica, the contribution of specific component to the surface energy is very important resulting in increased viscosity and Payne effect due to high filler-filler interactions. Different coupling agents can be used along with the silica filler in order to minimize the contribution of the specific component and maximize the dispersive component, resulting in improved filler dispersion. [1, 2]

3.4.2 Coupling Agents: Silanes

As mentioned before, compatibility between silica and rubber is poor due to polarity differences. Therefore, silane coupling agents are commonly used in tyre industry in order to enhance filler dispersion and thus, rubber-filler interaction leading to increased tyre performance. [2]

Silanes are bifunctional organosilicon compounds with general molecular structure X_3SiRY. RY represents an organofunctional group, i.e. mercapto or disulfide, with a short alkyl link with the silicon atom and it is responsible for providing bonding to the polymer during vulcanization. X represents an alkoxy group, i.e. OC_2H_5, which provides bonding to silicon atom through hydrolysis or condensation. [28, p.19; 34] A representation of silane general structure is presented in Figure 18. There are several organosilanes commercially available, being TESPT and TESPD the most widely used in tyre industry.

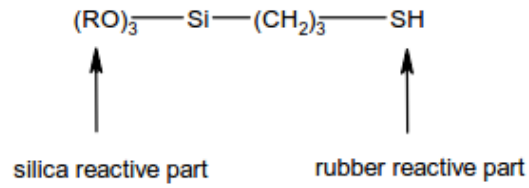

Figure 18. *Organosilane chemical structure. [35]*

Bis (triethoxysilylpropyl) tetrasufide (TESPT) is able to react with the polymer due to the poly-sulfide part and with the hydroxyl groups of silica surface due to the ethoxylsilyl-groups presents on silicon atoms. TESPT contains a sulfur average extent of 3.86 on the poly-sulfide part, releasing reactive sulfur fractions during processing of rubber compounds when TESPT is split. However, TESPT can also act as sulfur donor at high temperature or high shear conditions. [2] Figure 19 presents the chemical structure of TESPT and TESPD.

Bis (triethoxysilylpropyl) disulfide (TESPD) is an alternative to TESPT and is formed of a mixture of polysulfides. The sulfur average grade of TESPD is approximately 2 and additional elemental sulfur is required during processing to achieve similar

reinforcement capacity as TESPT. Nevertheless, TESPD presents higher stability at high temperature or high shear conditions. [14] Figure 19 presents the chemical structure of TESPD and TESPT.

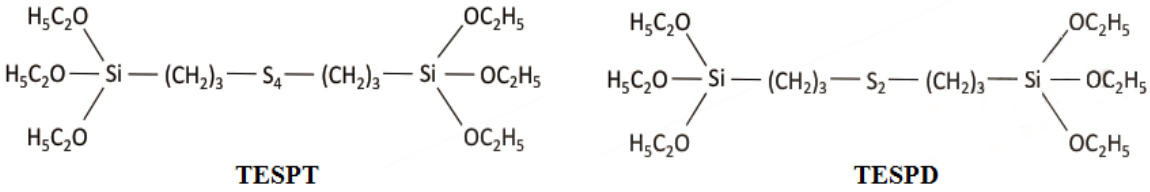

Figure 19. *Chemical structure of TESPT and TESPD coupling agents.*

3.4.3 Mechanism of silanization reaction

The reaction between silica and silane is called silanization and takes place in a two-step endothermic reaction. Previous to the primary reaction, silane molecules make contanct by adsorption with silica surface. During the *primary reaction*, the first ethoxy group quickly reacts with the germinal and/or isolated silanol groups on the silica surface as it is shown in Figure 20. [7] There are two different mechanisms to approach this primary reaction: by direct reaction of the alkoxy groups of the silanes with the silanol groups of silica surface or by hydrolysis of the alkoxy groups with a subsequent condensation with silanol groups.

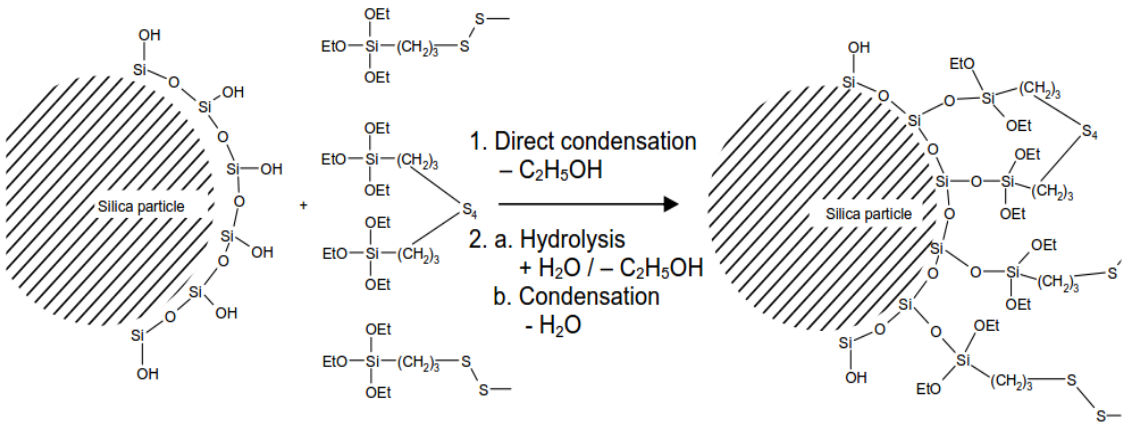

Figure 20. *Primary reaction of silanization mechanism. [1]*

In the presence of water, these reactions decrease remarkably their rate constant. Additionally, temperature directly affects to the rate constant of hydrolysis reaction by increasing its value at higher temperatures. Acidic or alkaline medium can be used as catalytic agents. After hydrolysis, the silane is activated and reacts with the silanol groups present on silica surface in a reasonably faster reaction than hydrolysis, making hydrolysis the limiting step of silanization reaction. This reaction is considered to follow a pseudo-first order kinetic law. [1, 2]

Right after the primary reaction, the *secondary reaction* takes place as consequence of unreacted ethoxy groups of silanes. [2] This reaction consists of a condensation reaction of the adjacent molecules of silanes on silica surface or between the alkoxy groups of silanes with silanol groups of silica filler. Additionally, it is well-known that a hydrolysis step is involved in this secondary reaction. [1] Figure 21 represents the secondary reaction between silica and silane.

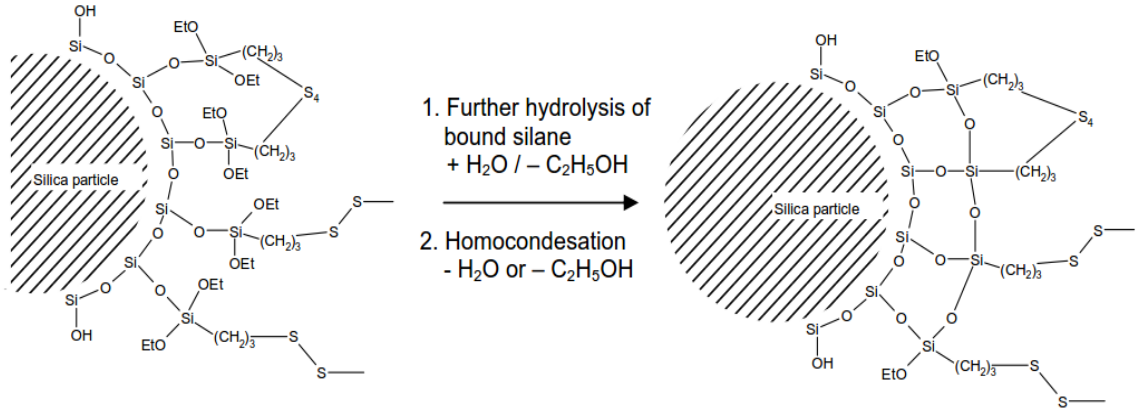

Figure 21. *Secondary reaction of silanization mechanism. [1]*

This secondary reaction is fairly slower than the primary reaction. Silanization reaction can be accelerated based on the rate of hydrolysis of the alkoxysilanes. It is possible to accelerate hydrolysis by using an acidic or basic catalyst as well as in the presence of moisture without affecting the final properties of the compound. The activation energy of both reactions ranges from 30 to 50 KJ/mol. [1, 2] Additionally, amines, enamines and aldimines have shown their potential to accelerate such reaction. Particularly, 1,3-diphenylguanidine (DPG) has demonstrated its strong capacity of improving the degree of silanization. [9]

3.4.2.2 Silane-rubber coupling reactions

It is well-known that silica-rubber reaction only occurs during vulcanization process, so that curatives and accelerators have great influence on the activation of such reaction. [2] Generally, the silica-rubber reaction is activated by a sulfur group such as poly- or disulfidic group or a blocked sulfur group. In addition, other functional groups can be used to create links between rubber and silane. These functional groups include double bonds which require activation by an active sulfur compound or by the generation of a radical fraction to produce simultaneous crosslinking of silane and polymer during curing. [1] Silane rubber reaction is illustrated in Figure 22.

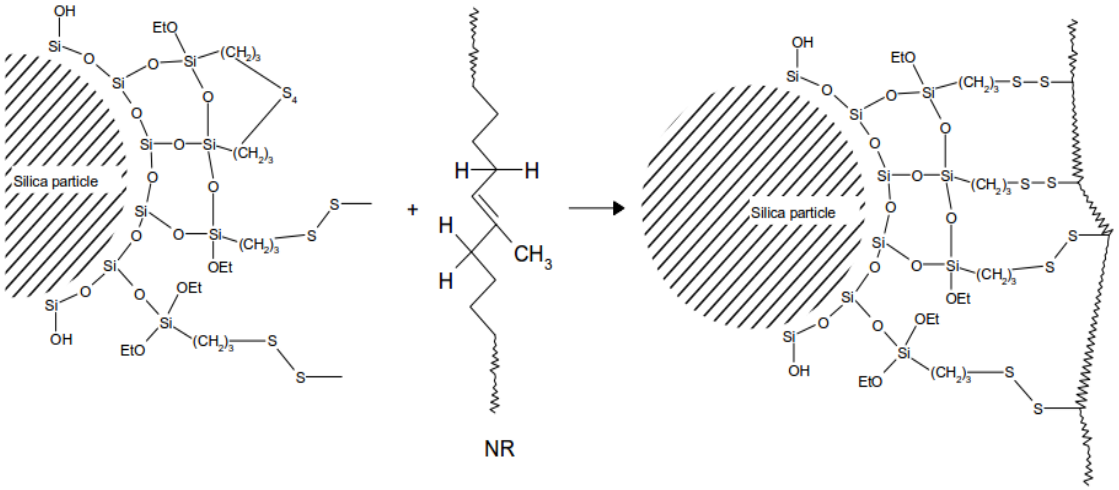

Figure 22. *Silane-rubber coupling reaction general scheme. [1]*

Right after the split of the sulfur groups, radicals or other active sulfur fractions are formed due to the unstable character of the polysulfidic groups of silanes creating silica-silane-rubber bonds. Görl et al. after studying the silane-rubber reaction, proposed a mechanism in which a disulfidic group activates the reaction of silanes forming an intermediate polysulfide that bonds to the silica filler. The intermediate polysulfide bonds to the polymer chain replacing the allylic hydrogen atom and the disulfidic group accelerating the reaction is released. Thereafter, the filler-polymer bond is formed. [1]
N-cyclohexylbenzothiazole-2-sulphenamine (CBS) is widely used as primary accelerator for the silane-rubber coupling reaction. [2]

3.4.3 Silica versus Carbon black as reinforcing fillers

Carbon black and silica are the most used reinforcing fillers in tyre industry. Properties of both fillers differ greatly from each other resulting on different reinforcing capabilities. When comparing silica and carbon black, the most perceptible difference is the weaker filler-polymer interactions of silica filler and the stronger tendency of filler particles to interact with each other. This characteristic of silica leads to poor filler dispersion resulting in an increased viscosity of the compound, lower modulus at high strain amplitudes, higher modulus at low strain amplitudes and low formation of bound rubber. Nevertheless, the use of coupling agents along with silica significantly enhances its reinforcing capability compared with carbon black affecting to numerous mechanical properties including: resilience, heat build-up, tear resistance, abrasion resistance, heat resistance, tack, shore hardness, stiffness, modulus and flex stability. [1, 8]

Due to the greater reinforcing capability of silica it is possible to decrease the filler content during compounding without adverse effects on the final properties of the material. In addition, the increased ratio of elastic component to damping filler of silica leads to a reduction in rolling resistance of tyres. [1, 8]

Silica-polymer networks present lower loss modulus (G'') than carbon black-polymer networks due to lower breaking and reformation rates during deformation cycles. Storage modulus (G') of silica filled rubber is also enhanced resulting in a lower phase angle (tan δ = G''/G'). Since both loss modulus and storage modulus are influenced by deformation, the phase angle increases at higher deformations. Figure 23 presents the temperature dependence of tan δ as well as the strain-dependence of loss modulus (Payne effect). [1, 8]

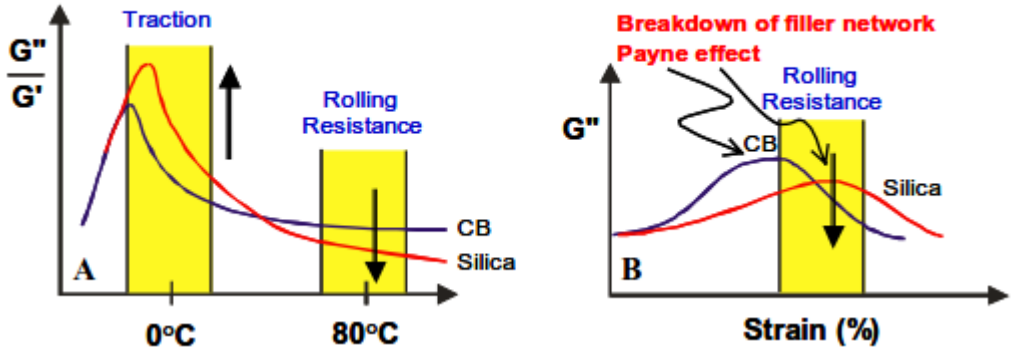

Figure 23. *Comparison of silica and carbon black mechanical properties. (A: tan δ dependence of temperature, B: Payne effect) [8]*

4. FILLER-POLYMER INTERACTIONS: RUBBER REINFORCEMENT

4.1 Reinforcement concept

The term rubber "reinforcement" is generally defined as the improvement of material properties such as tensile strength, abrasion resistance, tear resistance and modulus. Although the reinforcing mechanism of filled rubber is still not well defined, numerous investigations have been carried out to understand the reinforcing concept. After the study conducted by Payne (1965) on the strain dependence of filler-reinforced rubber, the Payne concept is commonly used to describe filler-filler and filler-rubber interactions in rubber compounds as it is illustrated in Figure 24. [35, 36]

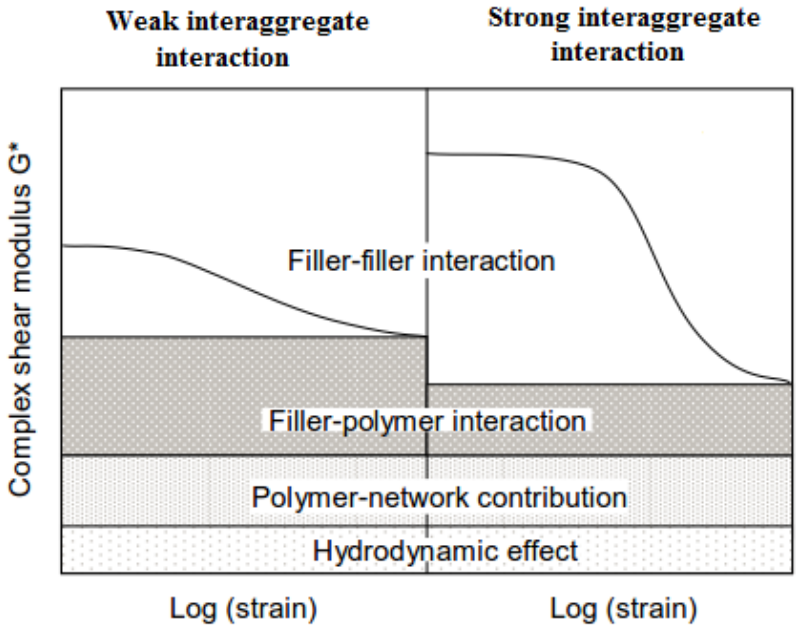

Figure 24. *Parameters affecting to shear modulus of reinforced rubber. [36, modified 7/2015 by M.Carmen Gamero]*

4.1.1 Filler-filler interactions: Payne effect

According to the so-called "Payne effect", the elastic modulus of a filled rubber strongly depends on deformation and significantly decreases at higher strain amplitudes. This behavior showed by filled rubber compounds results from the breakdown of the physical (London and Van der Waals) bonds created between filler particles during dynamic deformation. The Payne is a reversible effect showing great dependence on the filler

type but not on the rubber type. Moreover, it shows increased temperature dependence: at high temperatures, the initial modulus is decreased and consequently, the difference between storage modulus at high and low strains is reduced. Silica filler presents stronger interparticles forces than carbon black, thus, being the Payne-effect higher for this type of fillers. [35, 37]

A large number of models have been developed to explain the Payne effect. The quantitative model proposed by Kraus is based on filler agglomeration due to Van der Waal forces and deagglomeration due to Leronnard-Jones forces. According to this model, under periodic sinusoidal strain γ the interparticles forces are broken and reformed. [2, 38, 39] The breakdown rate R_{break} can be described as follows:

$$R_{break} = k_{bre}\gamma_o^m N_c \tag{2}$$

Where k_{break} is the breakage constant, $\gamma_o$is the maximum strain amplitude, N_c is the number of remaining contacts and m is the model fitting parameter.

The agglomeration rate can be expressed as:

$$R_{agg} = k_{agg}\gamma_o^{-m}(N_o - N_c) \tag{3}$$

Where k_{agg} is the agglomeration constant and N_o is the number of contacts elastically active at zero deformation.
This model proposes that storage modulus G' and loss modulus G'' of and aggregate network at specific strain can be expressed as:

$$\frac{G' - G'(\infty)}{G'(0) - G'(\infty)} = \frac{1}{1 + \left(\frac{\gamma_o}{\gamma_c}\right)^{2m}} \tag{4}$$

$$\frac{G'' - G''(\infty)}{G''(0) - G''(\infty)} = \frac{2\left(\frac{\gamma_o}{\gamma_c}\right)^{m}}{1 + \left(\frac{\gamma_o}{\gamma_c}\right)^{2m}} \tag{5}$$

where $G'(\infty)$ and $G''(\infty)$ are moduli at high strain amplitude and $G'(0)$ and $G''(0)$ at zero strain amplitude and $\gamma_c$is the strain half-width depending on filler type and concentration as well as on rubber matrix.
Another important model was proposed by Klüppel and it is based on the percolation and kinetic cluster-cluster aggregation theory. [40]

4.1.2 Filler-polymer interactions

Filler-polymer interactions, the so-called bound rubber, drastically increase the storage modulus G' with increasing filler load. [2]

Numerous models have been developed in order to explain the origin of filler-polymer interactions in filled compounds. [2] *Medalia* based his model on the rubber trapped between filler voids (occluded rubber) depending on the geometry of the different filler aggregates or agglomerates as it is shown in Figure 25 (a). These immobilized polymer chains behaves as large rigid particles without affecting to the elastic behavior of the rubber matrix at lower strain. At increased strain, the filler agglomerates and aggregates are broken releasing the entrapped rubber. [41]

The shell rubber model was developed by *Smith and Pliskin* and is attributed to the physical or chemical adsorption of polymer chains onto filler surface. This rubber layer attached to the filler surface shows an immobilized or glassy state character and is called "in-rubber structure", as shown in Figure 25 (b). [42, 43]

Thereafter, the glassy rubber shell model was proposed by *O´Brien et al*. based on the shell rubber model, which supports the idea of a glassy state layer and a rubbery state layer forming a double layer structure on the carbon black particles as illustrated in Figure 25 (c). [44]

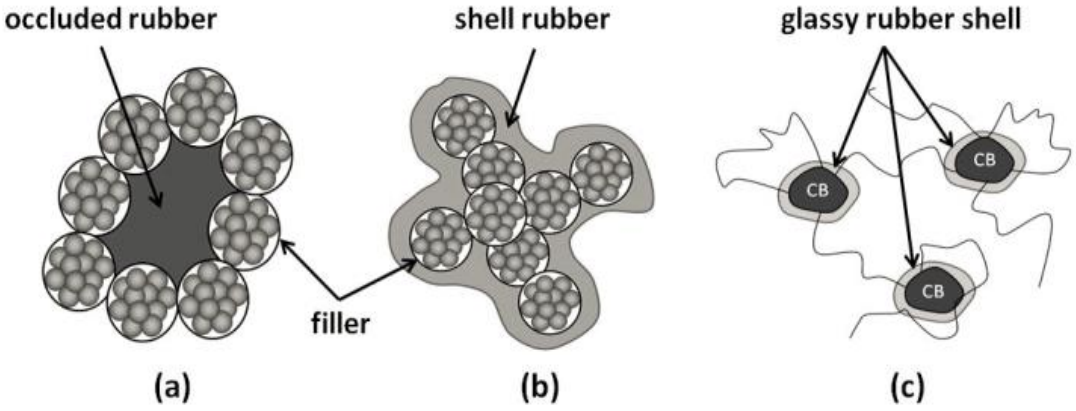

Figure 25. *Bound rubber models; (a) occluded rubber model, (b) shell rubber model, (c) glassy rubber shell model. [34]*

4.1.3 Polymer network effect

The strain-independent polymer network contributing to the shear modulus is dependent on the crosslink density formed during vulcanization and the nature of the polymer. The shear modulus (G_o) can be described as follows [2, 25]:

$$G_o = vkT \tag{6}$$

Where v is the concentration of elastically effective network chains per unit volume resulting from vulcanization, k is the Bolzmann´s constant and T is the absolute temperature. [2]

4.1.4 Hydrodynamic effect

The strain-independent hydrodynamic effect refers to the increment of the viscosity and moduli in a rubber compound with increasing filler load. The equation proposed by Einstein-Guth-Gold represents the behavior of the modulus of filled rubber with poor reinforcing fillers at small filler fractions (∅<0.3) [45]:

$$G' = G'_0(1 + 2.5\emptyset + 14.1\emptyset^2) \tag{7}$$

Where G' is the moduli of filled elastomers and G'_0 is the moduli of unfilled elastomers. $G'/_{G'_0}$ represents the strain amplification factor indicating the local strain produced by rigid fillers which cannot be deformed. Nevertheless, this equation is not valid for well-reinforcing fillers such as silica and carbon black since the modulus can reach higher values that those provided by Equation 7. [45]
Guth developed an equation for non-spherical particles including an adjustable shape factor (f) of the aggregates as follows:

$$G' = G'_0(1 + 0.67\, f\emptyset + 1.62 f^2\emptyset^2) \tag{8}$$

In this equation it is assumed that there is no chemical reaction between the filler particles and the medium. [46]

4.2 Dynamic mechanical properties of filler reinforced rubber

The dynamic mechanical properties of filled rubber directly influence the final performance of a tyre. Thus, the understanding of the theory of viscoelasticity is extremely important in tyre industry in order to reach favorable final properties of the rubber compounds. [2]

Rubber is a viscoelastic material, what means that while it is deformed part of the energy is stored elastically and the resting one is dissipated as heat into the material hysterically. This hysteric loss is not recoverable and contributes to the total drag force on a moving vehicle. [2, 8]

The energy applied to a viscoelastic material can be modeled at sinusoidal shear deformation $\gamma(t)$ of an angular frequency ω. [1, 47-50]

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{9}$$

Where $\gamma_0$is the maximum strain amplitude and *t* the time.
The shear response $\sigma(t)$ is also sinusoidal, but it is out of phase with the strain [47]:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) = (\sigma_0 \cos\delta)\sin\omega t + (\sigma_0 \sin\delta)\cos\omega t \quad (10)$$

Where σ_0 is the shear response at maximum strain and δ is the phase angle. This phase angle is graphically illustrated in Figure 26.

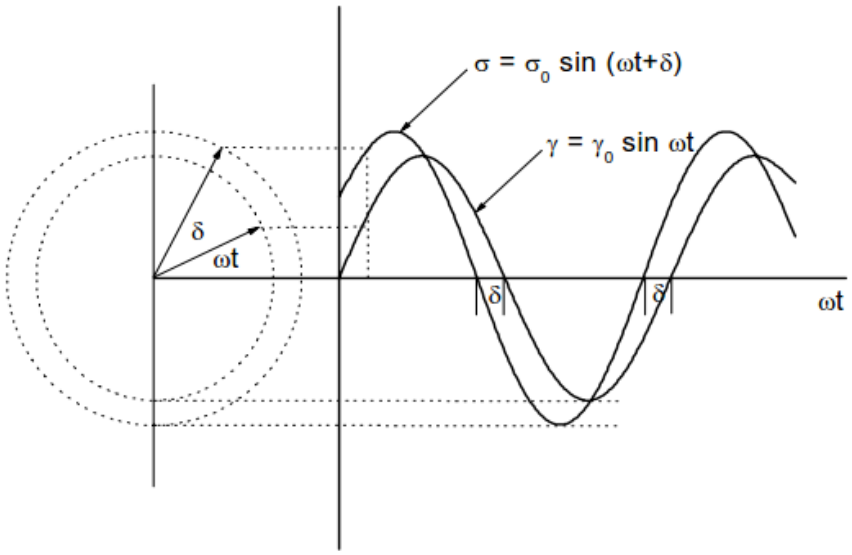

Figure 26. *Representation of the phase angle contributing to the delay of the shear stress response under sinusoidal deformation. [1]*

The shear stress signal $\sigma(t)$ can be divided into two different contributions: one in phase with the strain $\sigma_0 \cos\delta$ and the other 90° out of phase with the strain $\sigma_0 \sin\delta$. Both components can be defined by two moduli as follows:

$$G' = \frac{\sigma_0}{\gamma_0}\cos\delta \quad (11)$$

$$G'' = \frac{\sigma_0}{\gamma_0}\sin\delta \quad (12)$$

Where G' is the storage or elastic modulus, which is the component in phase and G'' is the loss or viscous modulus, which is the component out of phase with the oscillatory strain. By combining equations 11 and 12 it is possible to determine the correlation between strain and stress as follows [47-50]:

$$\sigma(t) = \gamma_0[\, G' \sin\omega t + G'' \cos\omega t] \quad (13)$$

These two components represent the real and the imaginary part of the shear modulus G^* when referred to a complex form [20]:

$$G^* = G' + iG'' \tag{13}$$

Or:

$$G^{*2} = G'^2 + G''^2 \tag{14}$$

The phase angle can be defined by using the storage G' and loss G''modulus as:

$$\tan\delta = \frac{G''}{G'} \tag{15}$$

Both G' and G'' have strong dependence on frequency and temperature. Figure 27 illustrates the frequency dependence of elastic and viscous modulus of a viscoelastic material.

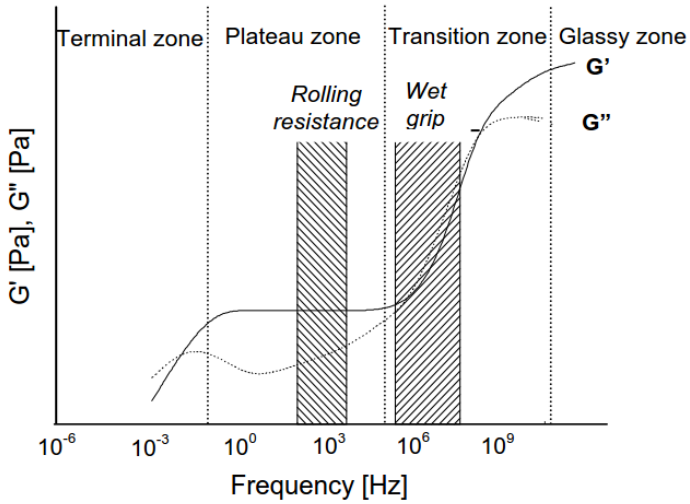

Figure 27. *Frequency dependence of elastic and viscous modulus of a viscoelastic material. [50]*

This frequency dependence is attributed to the mobility of chains and segment within the rubber material. At low frequencies, under one cycle of stress application the polymer chains are capable of following the applied strain without delay and energy loss. As long as the frequencies of the applied strain increase, the polymer chains reduce their ability to follow the applied strain and they start acting as temporary crosslinks, showing an elastic behavior. [1, 2] As consequence of the entanglement of polymers the resulting crosslink density is linked to the plateau region, in which the storage modulus is constant and there is a minimum in loss modulus. In this plateau region, the material still shows an elastic behavior and all type of movements are still possible.[2] Once the

frequency continues increasing, the material reaches a transition zone between the rubbery and glassy state in which the polymer mobility is strongly decreased and consequently, both storage and loss modulus heavily increase. Finally, at very high frequencies the material reaches a glassy state in which the polymer chains become rigid resulting on a very high modulus. At this zone the polymer chains do not show flexibility enough to follow the applied deformation and the dissipation of energy is remarkable with a maximum value of the loss modulus. [47-50]

As it can be seen from Figure 27, rolling resistance is within the rubbery zone as it is related to the loss tangent of rubber compounds at low frequency. However, wet grip refers to loss tangent at high frequencies and is within the transition zone between rubbery and glassy state. Normally, high wet traction is reached with higher loss tangent at high frequencies. [1, 52]

As mentioned above, the dynamic mechanical properties also depend on the temperature of the material which influences the mobility of the polymer chains. [1] Figure 28 presents the dependence on temperature of the storage modulus, loss modulus and loss angle.

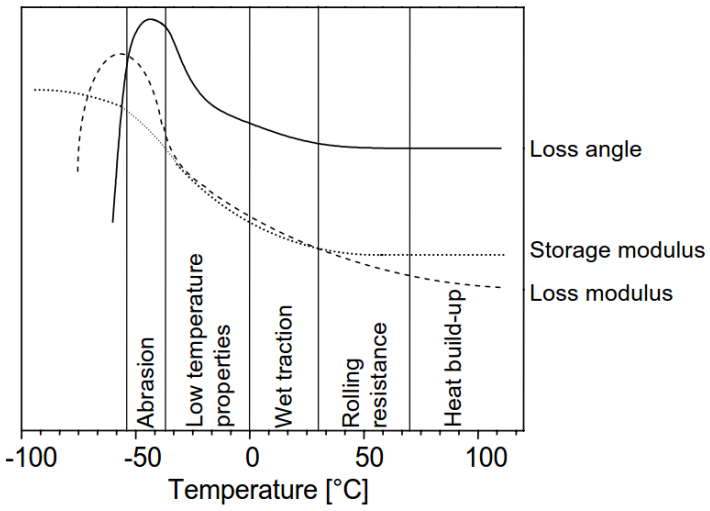

Figure 28. *Temperature dependence of dynamic properties of polymers. [1]*

As observed, when temperature is low and is close to the glass transition point, the phase angle shows a maximum and the polymer is in the glassy state with high moduli. After the glassy state, the polymer shows a rubbery state with high mobility of the polymer chain. Finally, the dissipation of energy is decreased and a plateau region is reached. [, 2, 8]

Generally, the glass transition temperature of the material is an indicator of the limit of its elastic behavior, so it can be used to predict the suitability of a tyre in winter conditions. [1, 2] The value of loss tangent at temperatures ranging from 0°C to +30°C is an indicator of the grip and traction properties on wet, icy or dry conditions. The running temperature of a tyre ranges from +30°C to +70°C, thus, at this temperature ranges the rolling resistance can be determined by the loss factor. When temperature exceeds

the running temperature range, the tyre is no longer operating at a safe region and reaching a region of maximum stress with consequent destruction risk. An estimation of the initiation of thermal decomposition is possible by evaluating the tan δ values at this temperature ranges since it is related with the heat build-up behavior. In this way it is possible to predict the range limit at which a tyre is able to offer a good and safe performance. [7]

The addition of fillers to the rubber matrix strongly affects the dynamic properties of filled rubber because of the interaction between the filler and the polymer. This filler-polymer interaction is affected by several parameters including, the filler type, filler particle size, surface activity and the amount of filler added to the rubber compound. [2] These parameters directly influence the formation and breakdown of agglomerations as well as the presence of bound rubber and occluded rubber. [1]

Carbon black and mainly silica are the most used fillers in the tyre industry. Figure 29 presents the variation of loss tangent with temperature within carbon black and silica filled compounds. [1]

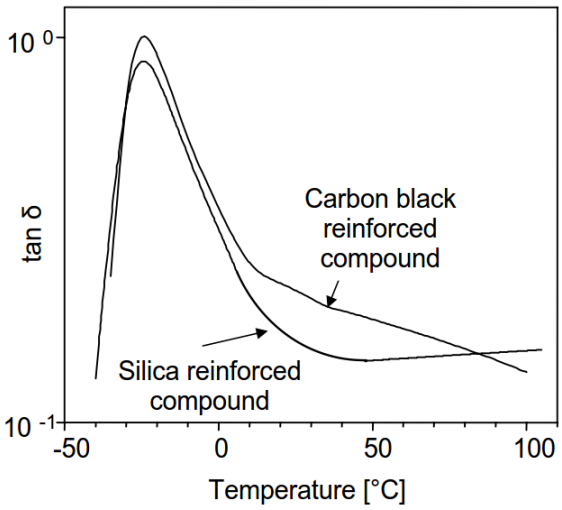

Figure 29. *Variation of tan δ with temperature on carbon black and silica filled compounds. [1]*

As it can be observed in Figure 29, the most significant difference between carbon black and silica filled compounds is the increasing phase angle of silica at higher temperatures. This increased phase angle using silica fillers refers to a reduced rolling resistance value in silica filled compounds. However, at low temperatures the loss tangent of silica filled rubber is higher than that of carbon black filled rubber, meaning that wet traction properties are also improved in silica filled compounds. The main reason of such differences between both reinforced compounds is the difference in surface properties of silica and carbon black fillers. Silanization reaction occurring with silica filled compounds leads to increased filler-polymer interactions by means of chemical bonds[1, 2, 8]

4.3 Bound rubber as result of rubber-filler interactions

Rubber compounds in tyre industry are reinforced with particulate fillers such as silica and carbon black by formation of bound rubber, which provides information about rubber-filler interactions. [52] The formation of bound rubber is a phenomenon still not very clear but it can be defined as the portion of rubber that cannot be extracted from uncured filled rubber after extraction with a good solvent. Bound rubber is the result of a combination of physical adsorption, chemisorption and mechanical interlocking. [23, p.81] Several polymer characteristics affect the formation of bound rubber, including the chemical structure and microstructure which directly influence the final properties of filled rubber, such as green strength, viscosity and cure characteristics. [52] Filler-rubber interactions begin in early stage of mixing in a non-instantaneous process with kinematical character where the viscosity increases with increasing bound rubber formation. First of all, good filler dispersion on the rubber matrix as well as good wettability of the filler particles are required for bound rubber formation. Elevated amount of mixing energy is needed to develop high amounts of rubber-filler interactions. [24] Figure 30 illustrates the model of bound rubber formation. A number of bound rubber models have been proposed by researchers as presented in previous section and bound rubber model of carbon black and silica are presented below.

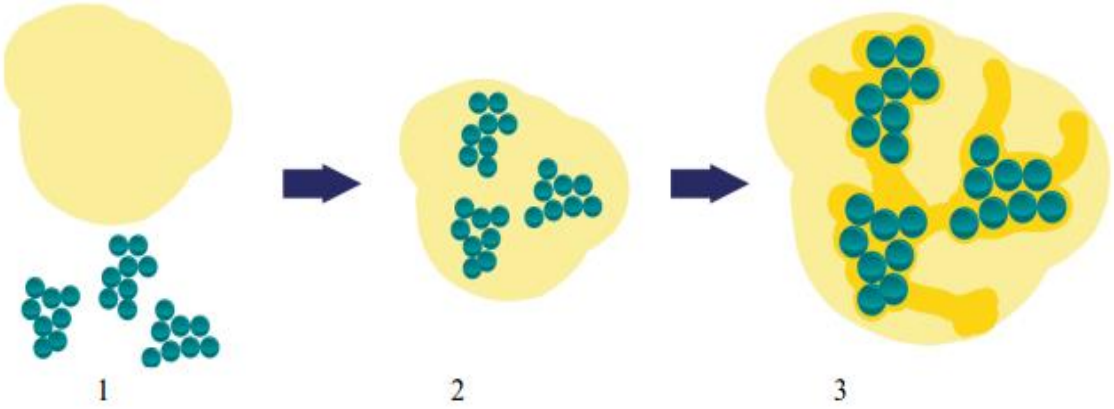

Figure 30. *Bound rubber formation model: (1) mixing of rubber matrix and filler particles, (2) wetting of filler particles by rubber and (3) formation of immobilized rubber, the so-called "bound rubber". [53]*

4.3.1 Bound rubber model of carbon black filled rubber

In carbon black filled rubber, carbon black particles fuse together after a proper mixing forming a grapelike arrangement where three regions can be differentiated as illustrated in Figure 31 [24]:

- *Region 1:* tightly attached to the filler surface there is a thin and rigid layer of polymer which behaves as the filler aggregate with restricted molecular motion.
- *Region 2:* it is formed by polymer chains bonded to the particles through the tightly bound rubber region, ultimately forming connective filaments between rubber-filler aggregates. This region is called loosely bound rubber and it is capable of undergo very large deformations showing flexibility.
- *Region 3:* it is formed by unbound rubber and no interactions between rubber and filler exist. This portion can be extracted from uncured compounds in the presence of a good solvent of the elastomer.

Increasing filler loads leads to three-dimensional aggregates of rubber-filler particles with diameters ranging from 50 to 100 nm and connected by soft polymer units. The loosely bound rubber surrounding the tightly bound rubber presents a thickness of approximately 3-6 nm. The thickness of the tightly bound rubber ranges from 0.4 to 1.3 nm, meaning that the formed bound rubber increases notably the diameter of the carbon black aggregates. This layer presents a very high modulus with an estimated concentration of carbon black of approximately 200 phr and the polymer chains are bonded randomly to the filler particles. [55]

The dynamic properties of the carbon black filled compounds are directly affected by the amount of bound rubber generated. The influence in Young´s modulus (E) is described by Guth-Gold equation [24]:

$$E_f / E_0 = 1 + 2.5\emptyset' + 14.1(\emptyset')^2 \tag{16}$$

Where $\emptyset'$is the effective volume fraction of the filler counting with the immobilized polymer fraction and E_f and E_0 are the Young's modulus of the reinforced material and the gum vulcanizate respectively. This correlation is valid for equilibrium or near equilibrium conditions. [24]

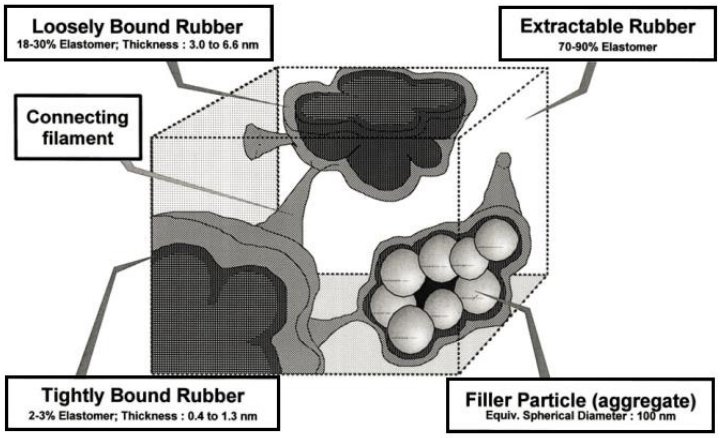

Figure 31. *Bound rubber model of carbon black filled rubber. [50]*

4.3.2 Bound rubber model of silica filled rubber

The bound rubber model of silica filled rubber as presented in Figure 32 establishes that silica aggregates fuse together to form a network by means of hydrogen bonding. Two main components can be distinguished: occluded rubber between the aggregates as well as chemically bonded bound rubber to the filler surface due to coupling agents. [2]

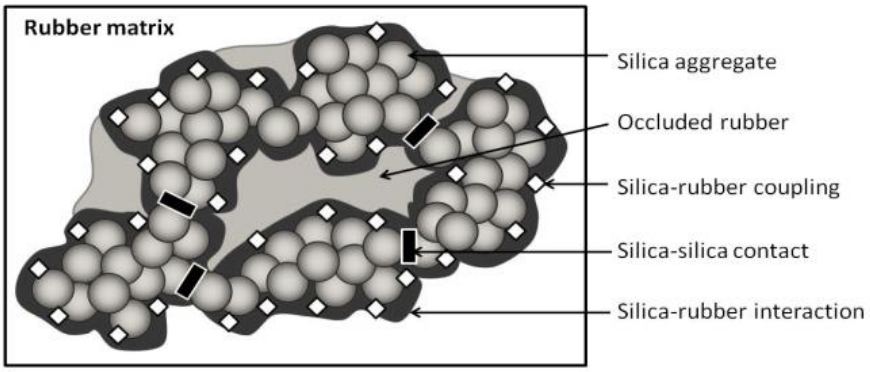

Figure 32. *Bound rubber model of silica filled rubber. [54]*

Luginsland et al. developed a simple model to explain the silica/silane reinforcing concept based on the differences in polarity between silica and rubber. As result, filler-filler aggregates are easily formed and part of the rubber is trapped between the filler network forming the so-called occluded rubber. This occluded rubber restricts the mobility of the trapped polymer chains. Nevertheless, under high deformations, the filler networks are broken, the occluded rubber is released and subsequently the rubber matrix is deformed. For that reason silane coupling agents play an important role in silica reinforcing potential, immobilizing the occluded rubber as well as the surrounding rubber onto the silica surface and thus, contributing to the modulus even under high deformations. [2,55]

5. TESTING OF RUBBER COMPOUNDS

When driving, many different obstacles such as objects, debris, potholes and ramps can appear on the road and the tyres of a car must be capable of overcome them in a safety way. Moreover, the tyre must be capable of transmitting the driving, braking and applied forces under both dry and wet conditions without producing extreme noise to the environment. The examination of the physical properties of the rubber compounds is crucial for the design, production, quality control and performance of tyres. For that purpose, a vast number of tests are implemented, including durability tests, quality control of materials and dynamic mechanical tests. [56, p. 7; 57, p. 2]

Besides, the study of filler-polymer interactions occurring within rubber compounds is extremely important in rubber industry since they influences directly the tyre performance related properties. In this chapter an overview of some conventional methods to asses rubber properties as well as some methods used to assess these filler-polymer interactions are presented.

5.1 Conventional testing methods to assess rubber compounds properties

After mixing, rubber compounds are subjected to a wide range of tests in order to evaluate their performance related properties and predict their further behavior ensuring good quality of the final product. Some of the most common conducted tests are presented in this chapter, including: Mooney viscometer, oscillating disc curemeter, rotorless shear curemeter, rotorless curemeter, stress-strain tensile testing, dynamic properties and some other methods to assess physical properties of rubber compounds. [58, p.20; 59, p.22]

5.1.1 Mooney viscometer

The Mooney viscosity test is one of the most common tests in rubber industry to measure the viscosity of the rubber compounds and is described in ASTM D 1646 or ISO 289 Part 1. [58, p.22] The Mooney viscometer consists of a grooved rotating metal disc (rotor) inside a sealed, pressurized and temperature adjustable die which is imbedded within the rubber samples. The rotor is grooved in order to avoid slippage of the rubber samples with the rotor or with the die surface. [58, p.20] According to the standards, the rotor speed should not be higher than 2 rpm for a specified time period in order to

avoid viscous heating. The resistance that rubber provides to the rotation of the disc is recorded as torque in Nm. [58, p.20; 59, p.22]

In rubber industry, several useful measurements can be performed using the Mooney viscometer, including Mooney viscosity, Mooney stress relaxation and pre-vulcanization characteristics.

5.1.1.1 Mooney viscosity

Mooney viscosity refers to the resistance to flow of the rubber at a low shear rates and provides important information regarding the molecular weight of raw rubber and the mixing quality of the rubber compounds. Normally, in this test the standard temperature according to ISO 289 is 100 °C and the preheating and running time may be specified. [61-63] A typical Mooney viscosity curve is presented in Figure 33. Generally, the Mooney viscosity test uses 1 minute of preheating followed by 4 or 8 minutes of running and the Mooney viscosity is recorded according to the minimum value reported within the last 30 seconds of the test. [59, p.22; 60, p.53]

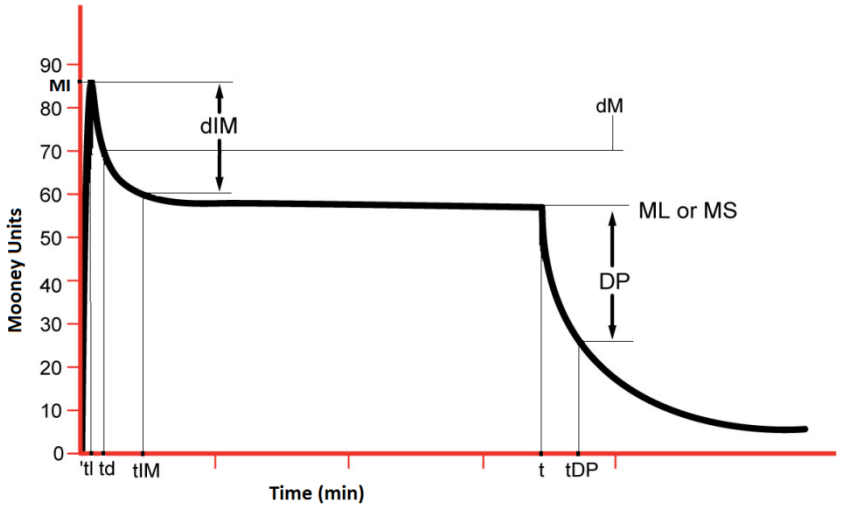

Figure 33. *Typical Mooney viscosity curve of a rubber sample. [59, p.23 modified 03/2016 by M.Carmen Gamero]*

5.1.1.2 Money stress-relaxation

According to ASTM D 1646, Mooney viscometer can be also used to measure the stress relaxation of rubber. During this test, after measuring the Mooney viscosity the rotor of the Mooney viscometer must be capable of stopping the rotation within 0.1 seconds and thus, the torque values are monitored just 1 second after the rotor stopped the rotation. These stress relaxation values follow a power law model which can be described as follows [58, p.26; 60, p.65]:

$$M = K(t)^a \quad (17)$$

where:

$M = Torque\ from\ Mooney\ stress\ relaxation$
$K = constant\ (torque\ 1\ s\ after\ the\ rotor\ stops)$
$a = rate\ of\ stress\ relaxation$

5.1.1.3 Pre-vulcanization characteristics

ASTM D 1646 also establishes that Mooney viscometer can be used to measure the scorch time of rubber compounds. The scorch test is useful to measure the onset of vulcanization after which the rubber compound becomes harder and it cannot be processed further. This test only allows detecting early stage of crosslinking since further stages lead to errors within the measurements because the crosslinked compound cannot longer flow and it tears. The temperature at which the measurements are conducted is selected according to ASTM D 1646 and based on the type of rubber subjected to the mentioned test. It is established that working at higher temperatures the cure reaction will be faster and consequently the scorch safety time will be shorter. [58, p.30; 63]

5.1.2 Oscillating disc rheometer

According to ASTM D 2084, the oscillating disc rheometer (ODR) presents some advantages over the Mooney viscometer, for example it is able to measure the state of curing as well as the scorch time and curing rate. The ODR presents a biconical rotor oscillating at small strain amplitudes which is imbedded into the rubber without rupture after closing the dies. Several important curing related parameters are obtained from the ODR curing curve, including: $M_L minimum\ torque$, $M_H maximum\ torque$, $t_s1\ scorch$, $t_s2\ scorch$, $t'10\ cure\ time$, $t'50\ cure\ time$, $t'90\ cure\ time$. [58, p.31; 60, p.53; 61]

5.1.3 Moving die rheometer

ASTM D 5289 contains the standards for the moving die rheometer (MDR) which was introduced in the rubber industry after the ODR to overcome the problems with the biconical rotor, whose lower plate tends to oscillate respecting the stationary upper die. The advantage of the MDR over rheometers containing rotor is a better temperature recovery time for the rubber compounds being tested, resulting in shorter scorch times. In addition, values of MH and ML tend to be higher with the ODR than MDR, since presents MDR higher test sensitivity. [58, p.34; 60, p.53]

5.1.4 RPA

The Rubber process analyzer (RPA), according to ASTM D 6204, was introduced in the rubber industry after the MDR and presents some favorable points with respect to MDR. RPA is one of the most used methods for measuring viscoelastic properties of rubber compounds before, during and after curing in versatile test configurations (wide ranges of temperatures, strains and frequencies). [62] The measurements provide important information about processability, cure characteristics and final cured properties. [58, p.40; 59, p.25] It is based on the application of a sinusoidal strain to an uncured rubber sample as it is shown in Figure 34. Moreover, with RPA the rubber specimens for testing can be loaded and unloaded in an easy manner and numerous valuable parameters can be recorded, including [58, p.40; 59, p.25; 62]:

- ***Elastic torque (S´):*** it refers to the elastic part of the rubber and is the value of the torque response which is in-phase with the applied strain.
- ***Viscous torque (S'');*** it refers to the viscous part of the rubber and is the value of the torque response 90° out-of-phase with the applied strain. It is a useful parameter to calculate the real dynamic viscosity.
- ***Tangent δ:*** it refers to the ratio of the viscous part divided by the elastic part. It is an important parameter giving information related to the processability of the uncured rubber as well as the hysteresis and resilience behavior of the cured rubber.
- ***Storage Modulus (G') and Loss Modulus(G''),*** which can be calculated from S' and S'' as follows:

$$G' = k \,.\frac{S'}{strain} \tag{18}$$

$$G'' = k \,.\frac{S''}{strain} \tag{19}$$

Where k is a constant dependent of the geometry of the die.

The complex shear modulus is calculated from G' and G'' as:

$$G^* = \left[(G')^2 + (G'')^2\right]^{1/2} \tag{20}$$

- ***Dynamic Viscosity:*** Real Dynamic Viscosity (η'), "Imaginary" Dynamic Viscosity (η'') and Complex Dynamic Viscosity (η*) which are calculated as follows:

$$\eta^* = G^*/\omega \tag{21}$$

Where ω refers to the frequency of the applied sinusoidal strain in rad/s.

$$\eta' = G''/\omega \tag{22}$$

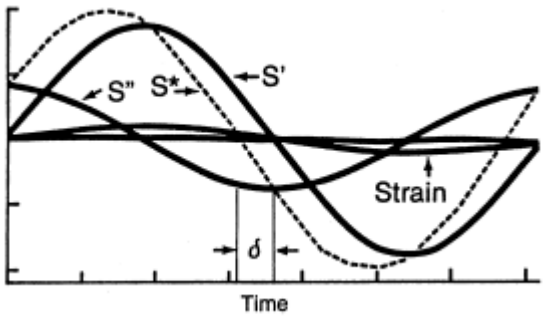

Figure 34. *Sinusoidal strain applied by RPA and strain response. [59, p.25]*

5.1.5 Tensile Properties

ISO 37 gives the standards for tensile test of rubber compounds which provides direct information about the curing conditions and whether the compound presents the correct amount and types of ingredients. Tensile test consists of pulling apart a previously cut dumbbell specimen of the tested rubber compound. ASTM standards establishes the use of specific grips to pull apart the dumbbells specimens and a rate of 500 mm/min to a final distance of minimum 750 mm. Tensile properties are the most commonly measured properties of cured rubber and from a single tensile test it is possible to monitor values of 100% and 300% elongation, elongation at break and stress at break. The ultimate tensile strength and elongation values are obtained from the rupture of the dumbbell specimen. Tensile test is a destructive test related to the strength of the rubber compound. Within filled vulcanized rubber the tensile properties are a direct indicator of filler dispersion within the rubber matrix and thus, the fillers reinforcing potential. [58, p.48; 60, p.55; 63] For example, variations in the ultimate tensile strength values may indicate unappropriated filler dispersion during the mixing stage. A typical stress-strain response of a filled vulcanized rubber is presented in Figure 35.

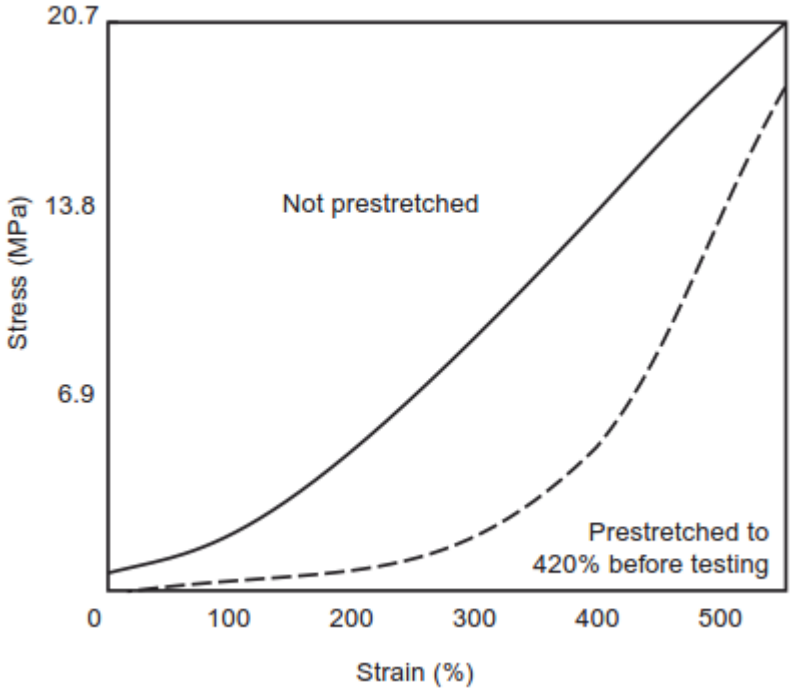

Figure 35. *Stress-strain response of a filled vulcanized rubber. [60, p.56]*

5.1.6 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) gives information about the viscoelasticity of rubber compounds by applying sinusoidal stresses to the samples. The tests can be performed under tension, compression, shear or 3-point bending and can be function of temperature, frequency or strain. DMA determines the storage modulus (G'), the loss modulus (G'') and the damping coefficient (tan δ) as a function of temperature, frequency or time. [64-66]

Low values of tan δ indicates that the cured rubber presents good resilience, while relatively high values of tan δ indicates high heat buildup. The study of the dynamic mechanical properties of rubber compounds is very common in the tyre industry for quality control or product development since DMA provides information about the transition regions. [58, p.49, 61]

5.1.7 Other cured Physical Properties measurements:

Several conventional tests are commonly performed to cured rubber compounds in rubber industry in order to assure good performance of the final product. These conventional methods are presented below.

5.1.7.1 Tear resistance

ASTM D 624 or ISO 34-1 refer to the standards used for tear resistance measurements. This test states the force needed to pull apart a rubber specimen using a tensile test machine following the mentioned standards. Apart from the well-established ASTM method some other methods to measure tear resistance are available as well as three types of tear specimens, including: die C, die B and trouser tear; the three of them are presented in Figure 36 in addition to the direction of the applied forces. As it can be observed, die C specimen is not previously nicked, while die B is nicked. The tear strength is the result of the sum of the energy required to stretch the specimen plus the energy required to tear it, leading to higher tear values than trouser tear specimens. [58, p.50; 60, p.64]

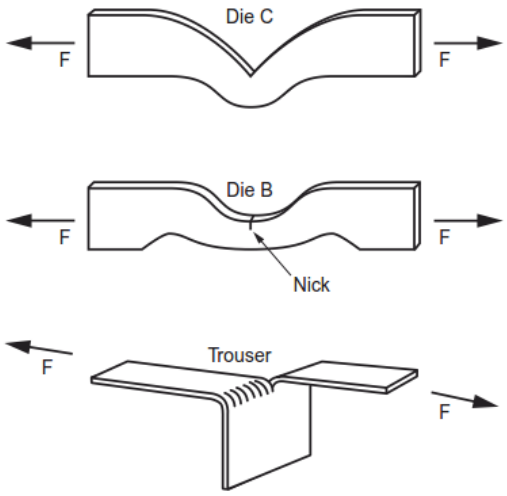

Figure 36. *Available specimens used in tear tests. [60, p.64]*

5.1.7.2 Hardness

ASTM D 2240 gives the standards to measure the hardness of rubber compounds. According to this standard, a durometer is used to measure the hardness of cured rubber samples by penetrating them with a special indentor. This is a fast and not precise manner of measuring the crosslink density of the cured samples. [58, p.55; 60, p.54; 64]

5.1.7.3 Compression set

ASTM D 395 describes the standards for the compression set measurements of cured rubber samples. Two methods are available which measure the predisposition of cured rubber samples to take a set. Within the first method a constant force is applied and within the second method a constant strain is applied both of them under the standard conditions previously mentioned, being the second method the most commonly used. [58, p.54; 66]

5.1.7.4 Heat buildup

ISO 4666-3 describes the standards for measuring hysteresis within rubber compounds. Hysteresis of a rubber specimen refers to the energy loss occurring when the specimen is deformed and then released. Usually, hysteresis is measured as the increment of temperature in a rubber specimen when flexed, known as heat buildup. In addition, tan δ measured by RPA is used to quantify the heat buildup of rubber specimens. [58, p.52; 60, p.69; 66]

5.1.7.5 Abrasion resistance

Abrasion of a tyre is the result of the rupture of small rubber particles as consequence of friction between the tyre tread surface and the road surface under several different conditions and at different speeds and loads. ISO 4649 describes the standards for measuring the abrasion resistance of tyre tread compounds. According to this standard, the abrasion resistance of vulcanized rubber samples is measured by forcing the test piece against a rotating cylinder. The volume loss (mm^3) is quantified and compared with the original test piece in order to evaluate the abrasion. [58, p.55; 60, p.70]

5.1.7.6 Fatigue resistance

Fatigue is the result of repeating rubber flexing, generating small flaws that develop cracks on the rubber surface that grow until failure. Initially the crack propagation is slow until the crack becomes bigger. There are several methods available for measuring the fatigue resistance of cured rubber compounds, giving ASTM D 430 the standards for one of the most common methods. According to this standard, The DeMattia machine is used to measure the fatigue resistance by bending a rubber specimen. [58, p.53; 60, p.68]

5.2 Characterization of filler-rubber interactions

Characterization of filler-rubber interactions is very important in tyre industry in order to understand the reinforcement mechanism of fillers in rubber compounds and thus, optimize tyre properties and performance. Filler-rubber interactions can be assessed by many different methods, some of them are presented in this section.

5.2.1 Measurement of the cure characteristics

The study of flocculation is highly important for the estimation of the effect that re-agglomeration has on the final properties of the materials. It is well known that flocculation may happen at the beginning of vulcanization. This study will pay special attention

to the initial phase of vulcanization in order to assess the extent of silica flocculation within the rubber compounds. Figure 37 reflects a typical curing curve where flocculation is taking place at the beginning of vulcanization.

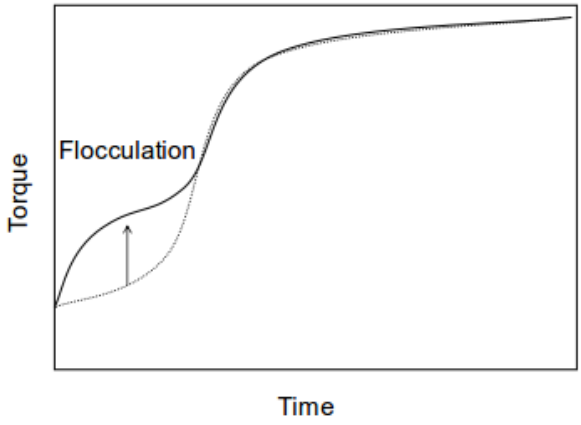

Figure 37. *Typical curing curve with flocculation. [2]*

5.2.2 Flocculation kinetics measurements

In silica filled rubber compounds, silica aggregates have strong tendency to self-associate and flocculate due to poor compatibility between silica and rubber caused by polarity differences. This flocculation mainly occurs during storage or at the beginning of vulcanization and results in a reduction of the reinforcing efficiency of the silica fillers. It is possible to study and evaluate silica dispersion in rubber matrix by determining the change in storage modulus of uncured compounds under simulated vulcanization conditions at low strain amplitudes. This study provides valuable information regarding the mechanism of fillers reinforcement which greatly influences the physical properties of rubber compounds. [2] In this thesis, an evaluation of the magnitude of filler-rubber interactions in silica filled rubber compounds is carried out by an advanced polymer analyzer (APA), measuring the kinetics of the silica flocculation within rubber compounds which can be described as a first order reaction by a simple model equation as follows [34]:

$$k_a = \frac{\ln(1-x_1) - \ln(1-x_2)}{t_2 - t_1} \; [min^{-1}] \tag{23}$$

$$lnk_a = \ln(k_0) - \frac{E_a}{RT} \; [KJ/mol] \tag{24}$$

Where k_a is the rate constant, t is the heating time, T is the heating temperature and E_a is the activation energy of the silica flocculation.

The silica flocculation can be calculated by monitoring the changes in storage modulus G´ of uncured silica filled rubber compounds without curatives during heating

at different temperature ratios at low strain amplitude. The degree of flocculation (x) can be expressed by the ratio of the Payne effect at time t and at infinite time [67]:

$$x = \frac{G'(t) - G'(i)}{G'(f) - G'(i)} \tag{25}$$

Being $G'(t)$ the storage modulus after a certain heating time t, $G'(i)$ the storage modulus after preheating and $G'(f)$ the final storage modulus.

The activation energy of the silica flocculation can be obtained from the slope of the straight line given by the Arrhenius plot, where the flocculation rate constant k_a is plotted versus the inverse of the temperature $1/T$ on a logarithmic scale. This slope provides values of the activation energy divided by the gas constant E_a/R. [2, 67]

5.2.3 Payne effect measurements

As reviewed in previous chapters, fillers within the rubber matrix tend to aggregate forming filler networks which usually break up during stress softening at small deformations. This phenomenon is the so called Payne effect and is an indicator of the filler interparticle forces. [1]

The study of Payne effect in filled rubber compounds provides direct information about the degree of dispersion of the fillers within the rubber matrix as well as hydrophobation efficiency of the used silane. Thus, Payne effect plays an important role in understanding the fillers reinforcement mechanism. [1, 2] Within this thesis, Payne effect is measured from a rubber process analyzer by monitoring the change in storage modulus at strain sweep at a constant frequency and temperature.

5.2.4 Bound rubber measurements

As described in previous chapters, silica fillers and rubber strongly tend to flocculate due to polarity differences and even when silane coupling agents are added this phenomenon may occur. Nevertheless, the addition of silane coupling agents increases the interfacial layer between the filler and the polymer reducing the polarity differences between them. Hence, bound rubber measurements of uncured samples without any curatives might allow an estimation of the magnitude of the filler-rubber interactions. From bound rubber measurements it is possible to evaluate either physical and chemical linkages or only chemical linkages by an ammonia treatment, however, for the present purpose both physical and chemical linkages are considered. [2]

The bound rubber measurement is performed by extracting the unbound rubber with toluene solvent for 96 hours at room temperature in a normal atmosphere. The bound rubber is calculated by the following equation:

$$BDR\ (\%) = \frac{m_0 - (m_2 - m_3)}{m_0}.100 \tag{26}$$

Where:

$$m_0 = rubber\ content\ in\ the\ sample, \quad m_0 = (m_2 - m_1).\frac{100}{total\ formulation\ (phr)}$$

$$m_1 = empty\ filter\ bag$$

$$m_2 = filter\ bag + unextracted\ sample$$

$$m_3 = filter\ bag + extracted\ and\ dried\ sample$$

5.2.5 Pyrolysis GC/MS

Analytical pyrolysis gas chromatography / mass spectrometry (PY GC/MS) is a technique widely used for many decades to study the microstructure and degradation mechanism of elastomeric materials. Normally this measurement is carried out on the bound rubber obtained from previous measurement in order to estimate the content ratio between BR/NR on the bound rubber layer. The operating principle of this technique is based on the application of heat to the material in order to break the bonds between the polymer chains producing small volatile particles which are analyzed by GC/MS. The conditions of PY GC/MS are controlled in a reproducible manner, so that the original polymer will always have a characteristic fragmentation pattern. [69-71]

Working principle

The vertical pyrolyzer is interconnected with the GC/MS and the pyrolysis starts after a sample located in the sample carousel is dropped to the preheated furnace. During pyrolysis, degradation takes place due to the breakdown of the weakest chemical bonds of the compounds releasing free radicals. These decomposition products are separated by injecting an inert gas, helium, which transports them in the vapor phase to the GC column. [73, 74]

Within the GC column, the degradation products are separated according to their interaction between the inert gas (mobile phase) and a stationary phase of the column. As a result of this interaction each degradation product is eluted at a specific time (retention time). [73, 74]

The GC column is interconnected with a MS responsible for the detection and identification of the compounds. The MS uses an ionization method (electron impact) which produces electrons by heating a wire filament with electric current. These electrons are bombed to the molecules coming from the GC when accelerated to approxi-

mately 70 eV following the next reaction: $M + e^- \rightarrow M^{+\cdot} + 2e^-$. From this reaction radical ions are released forming fragment ions which are detected and identified by comparing the fragmentation pattern with an existing database. [73, 74]

Pyrolytic degradation products from NR and BR

- **Natural Rubber**

Natural rubber is a polymer originated from natural sources and composed of compounded and cross-linked cis-isoprene (cis-2-methyl-1,3-butadiene) units. The mass spectral analysis after pyrolytic degradation of natural rubber shows that the major peaks correspond to isoprene and dipentene units as presented in Figure 38. [75]

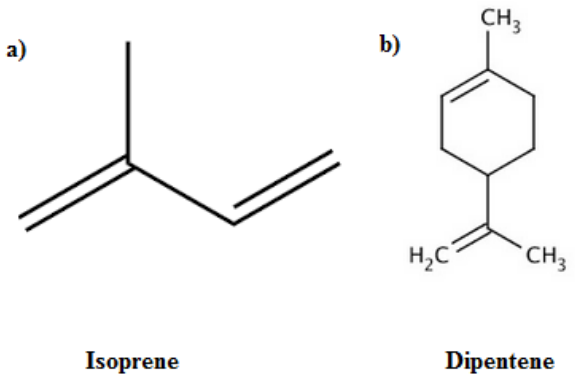

Figure 38. *Major pyrolyzates from NR.*

The peak areas of these degradation products in the pyrogram are studied to identify the amount of natural rubber present in the different rubber compounds.

- **Butadiene Rubber**

Polybutadiene rubber is a synthetic rubber formed by chemically linking multiple butadiene units forming a large polymer. The mass spectral analysis after pyrolytic degradation of butadiene rubber shows that the major peaks correspond to 1,3-butadiene and 4-vinylcyclohexene as shows Figure 39. The study of the peaks intensities of these two pyrolyzates provides useful information for quantitative analysis. [76]

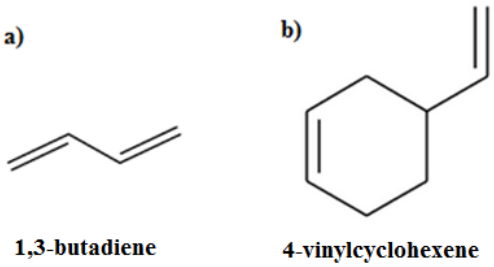

Figure 39. *Major pyrolyzates from BR.*

6. EXPERIMENTAL WORK

The main aim of this thesis is to find different measuring techniques useful to assess the filler-polymer interactions occurring within rubber compounds. Many different methods are available to detect those filler-rubber interactions, but this thesis is only focused on some of them, including bound rubber tests, flocculation tests, Payne effect measurements, tensile tests and some typical conventional tests. This experimental work will describe in a detailed way, firstly, the methods used for preparing the rubber compounds and secondly, the previously mentioned measuring techniques and conditions used to evaluate the extension of filler-polymer interactions.

6.1 Preparation of rubber compounds

In the present study, three series of compounds were formulated with different variable parameters within either their composition or their mixing times compared to the reference compounds. There were two reference compounds in Series A and Series B, with and without silane coupling agent as presented in Table 3, while in Series C only one compound with silane is taken as reference.

6.1.1 Recipes

Due to confidentiality reasons, some information regarding the recipes of the compounds is missing and only simplified versions are given. Table 3 lists the most remarkable ingredients in the recipe of the batches used as references within this thesis.

Table 3. *Formulation of the reference compounds*.

Compound	Elastomers (NR/BR) (phr)	Carbon black (phr)	Silica (phr)	Silane (phr)	DPG (phr)
Reference 1	100	10	60	4	1
Reference 2	100	10	60	-	1

As it is shown, the reference compounds differ just on the addition of silane coupling agents. The important role of silane coupling agents on filler-rubber interactions will be

also evaluated and for that purpose one reference compound without silane was formulated.
Natural rubber and butadiene rubber in different amounts were used for all the batches. In addition, both carbon black and silica reinforcing fillers were added to the recipes but as mentioned in previous chapters, this study is principally focused on silica filled rubber so that silica was considered the reference filler. The accelerator used for the reference compounds was DPG.

6.1.2 Compound development approach

As the principal target of the present study is to find different methods to assess filler-polymer interactions several approaches have been followed for that purpose. Numerous variations to the reference formulations have been considered within the different series in order to investigate and detect their influence on filler-filler and filler-polymer interactions. The approaches used for each series are presented in Tables 4, 5 and 6. These tables summarize the different variations made to the original recipe of the reference compounds of each series.

Table 4. *Variations made to the parameters of the reference formulations in Series A.*

Series A	
Batch	**Variable parameters**
RA.1	*Reference batch*
RA.2	*Reference batch without silane*
A.1	Variation of butadiene rubber →Functionalized butadiene rubber
A.2	Variation of silica type→Larger surface area silica
A.3	Variation of silane type→Trial mercaptosilane
A.4	Trial mercaptosilane + different accelerator
A.5	DPG added with curing package

As it is presented in Table 4, in Series A five different modifications were made to the recipe of the reference batches (*RA.1* and *RA.2*) in order to evaluate filler-polymer interactions.
Based on previous knowledge, it is known that functionalized butadiene rubber is capable of enhance filler-polymer interactions since the hydroxyl groups of silica particles present strong tendency to associate with the functionalized butadiene rubber. For that reason, in batch A.1 butadiene rubber was replaced by functionalized butadiene rubber.
Batch A.2 was prepared in order to detect how larger silica particles affect to filler-polymer interactions.
Batch A.3 was intended to replace the normal silane type by a trial mercaptosilane so that to get different kind of filler-polymer interactions to be tested and evaluated.

Batch A.4 replaced both normal silane type by a trial mercaptosilane as well as DPG by other accelerator type. This batch was prepared for trying to get an enhanced combination between the mercaptosilane and the accelerator so that stronger filler-polymer interactions may occur.
In batch A.5, DPG was added with the curing package instead of with the normal mixing program. The main purpose of this batch is trying to accelerate the silanization reaction and thus increase filler-polymer interactions.

As it will be presented in following chapter, Batch A.2 showed significantly adverse results compared to the compound reference A.1. For that reason, batch A.2 was considered as the reference compound in series B and C, which are focused on the improvement of filler-polymer interactions within the mentioned batch. With that intention several variations to its composition and mixing times were accomplished.
Similar to previous reference compounds of series A (*RA.1 & RA.2*), the reference compounds in series B were formulated with and without silane coupling agent (*RB.1 & RB.2*) in order to evaluate its role on the formation of filler-polymer networks.

As listed in Table 5, batch B.1 and batch B.2 were prepared with an increased DPG content in order to detect whether the accelerator is able to improve filler-polymer interactions when large surface area silica is used. DPG may be capable of accelerate the silanization reaction showing improved filler-polymer interactions.
Batch B.3 was prepared in order to assess how increased silane coupling agent contents affect to the filler-polymer interactions occurring when large surface area silica is used.
Batch B.4 replaced natural rubber by masticated natural rubber so that to detect whether lowering the viscosity of natural rubber may affect to filler-polymer interactions.

Table 5. *Variations made to the formulation of reference compounds in Series B.*

Serie B	
Batch	**Variation**
RB.1 (Batch A.2)	*Reference batch*
RB.2 (Batch A.2 ,no silane)	*Reference batch without silane*
B.1	Increased DPG content up to 200%
B.2	Increased DPG content up to 300%
B.3	Increased silane content up to 160%
B.4	Masticated Natural Rubber

Series C is intended to investigate the influence of the mixing extension on filler-rubber interactions of the batch Reference B.1. However, in this series no reference batch without silane was prepared. The mixing program used in this thesis is explained in section 6.1.3. Table 6 summarizes the variations of the mixing times accomplished in each batch of Series C.

Table 6. *Variations made to the mixing times of reference compound in Series C.*

Series C	
Batch	**Variation**
C.1	Decreased mixing time (40 sec in both stages)
RC.1(Batch A.2)	*Normal mixing (60 sec in both stages)*
C.2	Increased mixing time (80 sec in both stages)
C.3	Increased mixing time (100 sec in both stages)
C.4	Increased mixing time (120 sec in both stages)
C.5	Increased mixing time (140 sec in both stages)

6.1.3 Mixing

Due to confidentiality reasons the mixing program used within this thesis cannot be revealed, but a simplified version is described below. The mixer used was an internal *Krupp Elastomertechnik* with intermeshing rotors and with a theoretical volume of 1.7 dm^3.

The normal program *(Mixing program 1)* followed for all the mixed compounds consists of a one stage mixing of 180 seconds with 90 seconds of constant temperature phase at the end of the stage.

A variation in the mixing program is introduced in the batches where the conventional silane is replaced by a trial mercaptosilane (batches A.3 and A.5). This mixing program *(Mixing program 2)* consists of two mixing stages: the first stage consists of mixing during 120 seconds and a 120 seconds constant temperature phase at the end of the stage, while the second stage consists of 130 seconds mixing.

Both mixing programs include the constant temperature phase, where the temperature is increased in order for the silanization reaction of silica to occur *in situ*. All the batches of series A reached 145°C at this final constant temperature phase except batch reference A.1 that only reached 141°C. For series B and C all the batches reached a temperature of 145°C in the final constant temperature phase.

The curatives were added on a two-roll mill to all the compounds after they were let to settle down overnight. Prior to the curatives addition, the compounds were mixed during 130 seconds in order to warm them up and reduce the viscosity so that the best performance of the chemicals can be achieved.

6.1.4 Vulcanization

Vulcanization of the compounds is required for some testing methods, such as dynamic mechanical analysis and tensile test. The samples with curatives were vulcanized in an

hydraulical flat press MKH E 60 M at their corresponding t90 previously measured with RPA.

6.2 Conventional rubber compound testing

Mooney Viscosity ML(1+4)

For the unvulcanized compounds, the Mooney viscosity ML(1+4) was measured according to ISO 289 and using a Monsanto MV 2000E from Alpha Technologies. The measuring temperature was 100°C and the results given in ML(1+4), M referring to Mooney, L to a large rotor of the tester and (1+4) to 1 minute of preheating and 4 minutes of measuring time.

DIN Abrasion

A Zwick Roell abrasion tester was used to measure the abrasion resistance of the rubber samples following the standard ISO 4649. According to this standard, the abrasion resistance of vulcanized rubber samples is measured by forcing the test piece against a rotating cylinder with a diameter of 16 ± 0.2 mm. The oxide abrasive sheet is of grain size 60 and the dimensions are at least 400 mm wide and 474 ± 1 mm long. The distance of abrasion is normally 40 meters. The volume loss (mm^3) is quantified to measure the abrasion resistance of the material.

Rheometer

The curing characteristics of the compounds were measured using a Moving Die Rheometer MDR 2000 from Alpha Technologies and following the standards given by ISO 3417. Within this test, a round piece of approximately 5 grams is cut from a rubber sheet and the rubber flow as a response to an applied force is measured. The lower die oscillates at 1.66 Hz with a 0.5° angle. The test was performed at a temperature of 160°C for all the compounds and the duration of the tests was approximately 40 minutes.

Dynamic Mechanical Analysis (DMA)

As presented in section 5.6, Dynamic Mechanical Analysis (DMA) gives information about the viscoelasticity of rubber compounds by applying sinusoidal stresses to the samples. In this thesis a Gabo Eplexor 500 N in tension mode was used to measure the dynamic mechanical properties. The samples were prepared from a 2 mm sheet and the measurements were done using a static strain of 3%, a dynamic strain of ±0.2 %, and a contact force of 2 N. The frequency was kept constant at 10 Hz and the heating rate was 2 K/min. The temperature ranged from -70 °C to 70°C for all the compounds.

Rubber Process Analyzer (RPA)

In this thesis, a RPA 2000 from Alpha Technologies was used to measure the dynamic properties of uncured samples. The samples were cut in round pieces of about 5 grams and placed into the cavity. The measurements provided results regarding S'', S', S* and tan δ values at 60°C with a strain angle of 20°. Basically, the results of this test are useful for determining a reference point for the DMA results and properly assess the rolling resistance.

6.3 Methods to assess filler-polymer interactions

As described previously, the aim of this thesis is to find different techniques to assess the filler-polymer interactions occurring in filled rubber compounds. In chapter 5, the principles and theoretical background of the testing techniques were presented. In this section the methods and the parameters used are reviewed.

6.3.1 Bound rubber measurements

Bound rubber tests are implemented in order to detect the amount of bound rubber formed on the filler surface. The bound rubber measurement is performed by extracting the unbound rubber with toluene solvent for 96 hours at room temperature in a normal atmosphere. Both chemical and physical bound rubbers are taken into account in this measurement and the method used is as follows:

- A piece of approximately 0.2 grams of unvulcanized rubber without curatives was cut and placed into a filter bag. Five pieces of each sample were prepared.
- The filter bags were immersed into 250 ml of toluene for 96 hours at room temperature.
- Toluene was renewed every 24 hours.
- After 96 hours, the filter bags were extracted from the toluene and dried for 48 hours at room temperature.
- After the samples were completely dried, they were weighted and the amount of bound rubber was calculated according to Equation 26.

6.3.1 Flocculation studies

Flocculation can be evaluated by several methods. In the present study, two different techniques are used for that purpose; evaluation of the curing curves of the batches and calculation of the kinetics of flocculation at different temperatures. These techniques are presented below.

6.3.1.1 Measurement of the curing curves

The curing curves were measured by using an advanced polymer analyzer (APA 2000) from Alpha Technologies under the following conditions: temperature 150°C, 0.833 Hz and 0.2 % strain during 25 minutes. As it was documented in section 5.2.1, flocculation normally arises at the initial phase of vulcanization, so that a special emphasis was put to this initial increment of the torque in order to evaluate filler flocculation.

6.3.1.2 Measurement of the kinetics of silica flocculation

The flocculation kinetics of silica filled rubber compounds is commonly assessed by measuring the storage modulus G' at low strain amplitudes. At small deformations the filler-filler interactions directly contributes to the storage modulus, thus affecting the physical properties of the reinforced rubber. The kinetics of silica flocculation was monitored for the uncured rubber samples by using an advanced polymer analyzer (APA) from Alpha Technologies. The storage modulus was monitored at 0.28% strain amplitude and at temperatures ranging from 100°C to 140°C. The procedure was as follows:

- A circular piece of sample was cut with the cutter 2000R from alpha technologies and was placed into the APA.
- The sample was preheated during 1 minute at 100°C, 110°C, 120°C, 130°C and 140°C.
- The storage modulus was monitored at 0.28% strain amplitude and 0.5 Hz during *t90* of each sample, at constant temperatures of 100°C, 110°C, 120°C, 130°C and 140°C.

After following this procedure, the kinetics of silica flocculation is calculated according to the equations presented in section 5.2.1.

6.3.2 Payne effect measurements

As documented in theoretical part, Payne effect refers to the reduction of storage modulus of filled rubber with increasing strain amplitude due to the rupture of the filler-filler network. For that reason, the Payne effect is taken as a good indicator of the degree of filler-filler interactions in the rubber compounds.

Payne effect was studied with an Eplexor Gabo qualimeter 2000N because it provides high accuracy at very low strain amplitudes. The measurements were performed at a dynamic strain sweep with amplitudes ranging from 0.1% to 20%, at 10 Hz frequency and at a temperature of 21°C.

6.3.3 Tensile properties

The tensile properties of the vulcanized compounds were measured by using a Messphysik MIDI-10-20/4x11 tensile tester according to ISO-37. The specimens were cut into a dumbbell shape from a 2mm vulcanized sheet. The mechanical properties monitored with this method are tensile strength, elongation at break, stress at break, stress at 100% elongation and stress at 300% elongation.

7. RESULTS AND DISCUSSION

In this section, the results obtained in the experimental part of this thesis are presented and discussed. The results of each series of measurements are presented into separate subchapters. Firstly, the results of the conventional testing will be evaluated and finally the results of the testing conducted to assess filler-polymer interactions are discussed.

7.1 Results of conventional rubber compound testing

7.1.1 Series A

In this subchapter, the results of the conventional measurements performed for series A are discussed, including Mooney viscosity, DIN abrasion, curing characteristics and dynamic mechanical properties. Moreover, all the detailed results are collected in Appendix 1.

Recipe & mixing

The main target of this first mixing round was to evaluate the effect of some variations made to the formulation of the reference compounds on filler-polymer interactions. As mentioned before the recipes and the mixing programs are confidential, so that a simplified version is presented in Table 7.

Table 7. *Recipe and mixing programs of compounds in Series A.*

Ingredient [phr]	***RA.1***	***RA.2***	**A.1**	**A.2**	**A.3**	**A.4**	**A.5**
NR + BR (Type I)	100	100	-	100	100	100	100
NR + BR (Type II)	-	-	100	-	-	-	-
CB	10	10	10	10	10	10	10
Silica (Type I)	60	60	60	-	60	60	60
Silica (Type II)	-	-	-	60	-	-	-
Silane (Type I)	4	-	4	5	-	-	4
Silane (Type II)	-	-	-	-	5.5	5.5	-
DPG Accelerator (Type I)	1	1	1	1	1	-	1 (added with curatives)
Accelerator (Type II)	-	-	-	-	-	0.5	-
Mixing program 1	x	x	x	x	-	-	x
Mixing program 2	-	-	-	-	x	x	-

Mooney viscosity ML(1+4)

As it can be observed in Figure 40, the Mooney viscosity values obtained for batches in series A were all in the same line of values except for batches *RA.2* and A.2. These results were expected for batch *RA.2* due to the absence of silane coupling agent, what leads to increased formations of filler-filler networks resulting in increased viscosity of the compound. In addition, batch A.2 also presents a higher value of Money viscosity than batch *RA.1* since the silica used in its formulation presents larger surface area. Larger surface area silica results in strong interparticle forces, which negatively influence the processing behavior of the compounds due to increased agglomeration of the filler particles. Variations on the butadiene rubber type (batch A.1), silane type (batch A.3), variation of accelerator type along with different silane type (batch A.4) and addition of DPG accelerator within the curing package (batch A.5) seem not to affect to values of Mooney viscosity.

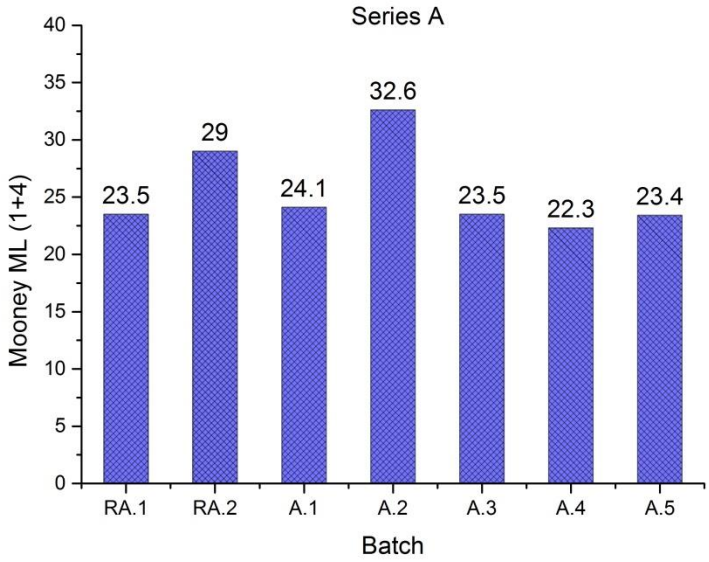

Figure 40. *Mooney viscosity values for batches in series A.*

DIN Abrasion

DIN abrasion test performed on filled rubber compounds is a good indicator of fillers reinforcing capability. Figure 41 illustrates the results of the DIN abrasion measurements of the compounds in series A. As it was expected, from this figure it can be noticed that batch A.2 presents the minimum volume loss. According to the theory, higher surface area fillers promote improved abrasion resistance. Batch *RA.2*, without silane coupling agent, presents the poorest abrasion resistance and the highest volume loss, indicating poor filler-rubber adhesion and poor filler dispersion. The use of silane type II (batch A.3 and A.4) affects negatively to the abrasion resistance of the compounds, increasing the material loss. Additionally, the addition of the DPG accelerator along with the curing additives (batch A.5) shows improved abrasion resistance results. This may be attributed to a better activation of the silanization reaction.

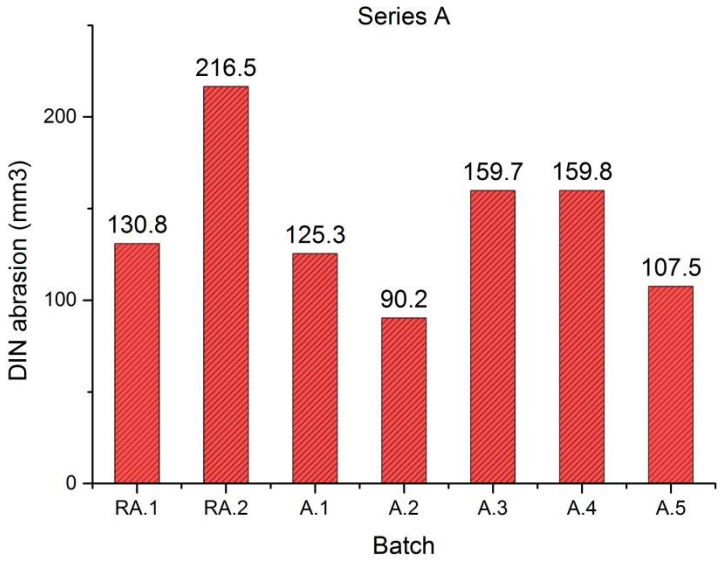

Figure 41. *DIN abrasion for batches in series A.*

Vulcanization characteristics

The vulcanization characteristics of the batches in series A are presented in Table 8. The values of *t10* and *t90* represent the time at which 10% and 90% of the total crosslinking has been achieved, while F_{min} and F_{max} values represent the minimum and maximum torque reached during vulcanization. As it can be noticed, the values of t10 of the batches vary widely compared to compound *RA.1*, being mainly affected by the lack of silane, the difference in silica surface area, different silane and different accelerator type. Mostly, the *t10* values of batches A.1-A.5 are drastically reduced compared to the *t10* value of batch *RA.1*. *t90* value is normally an indicator of the optimum curing time and as it is observed in Table 8, all compounds in series A show quite different values of *t90*, indicating different vulcanization characteristics. Batch A.1 and batch A.3 presents the highest and lowest values of *t90* respectively.

Table 8. *Vulcanization characteristics of compounds in series A.*

Batch	***RA.1***	***RA.2***	**A.1**	**A.2**	**A.3**	**A.4**	**A.5**
F_{min} (dNm)	1.1	1.5	1.1	2.1	1.0	1.0	1.1
F_{max} (dNm)	10.4	10.2	10.4	13.6	9.9	10.0	11.1
t10 (s)	8.3	4.5	8.4	3.6	3.6	5.3	6.4
t90 (s)	18.6	11.7	19.5	13.7	6.6	8.2	15.4

The values of F_{min} and F_{max} obtained from the RPA shows similar torques for all the batches in series A, indicating similar stiffness. However, batch A.2 presents higher

values of both F_{min} and F_{max} indicating higher stiffness of the compound when larger surface area silica is used.

Dynamic properties: tan δ

It is well known from the literature that tan δ at 60°C is a predictor of rolling resistance and is related to the extension of filler-filler networking, while tan δ at 0°C is a predictor of the skid behavior and traction of a tyre. Lower values of tan δ at 60°C indicate lower rolling resistance of a tyre and higher values of tan δ at 0°C refers to improved wet traction. As it was presented in the literature, the three most important properties of a tyre are rolling resistance, wet grip and abrasion resistance and a balance between them must be found to optimize its performance. These properties are conflictive and it is not possible to improve the three of them simultaneously. Normally, the improvement of rolling resistance tends to reduce the wet grip and durability of a tyre and for that reason, silica/silane technology is intended to introduce a balance between these properties.

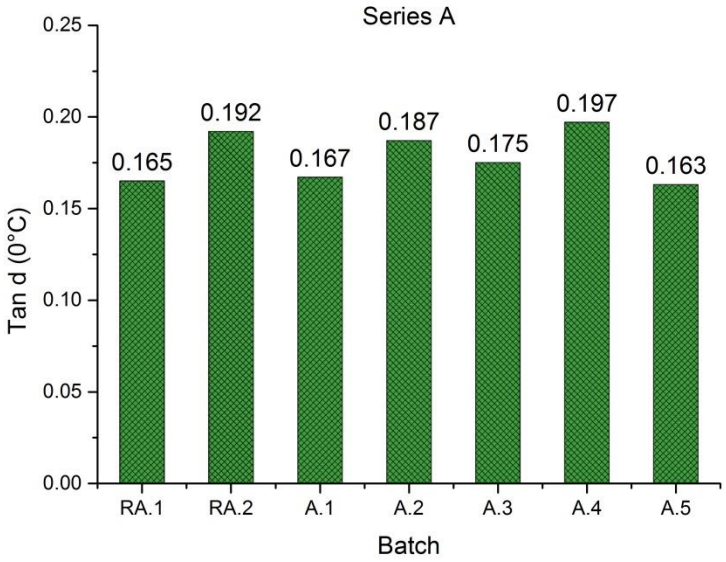

Figure 42. *Values of tan δ at 0°C for compounds in series A.*

Figure 42 illustrates the results of tan δ at 0°C obtained from the DMA for batches in series A. According to this figure, the most adverse results of wet grip as it was expected correspond to batches with absence of silane, with larger surface area silica and when using silane type II and accelerator type II (batches *RA.2*, A.2 and A.4). However, using butadiene rubber type II (batch A.1), using silane type II (batch A.3)and when accelerator is added with the curatives (batch A.5) seem not to affect significantly to the values of tan δ at 0°C when compared to the reference compound. Normally, wet grip increases when rolling resistance increases and an optimum between both values must be encountered.

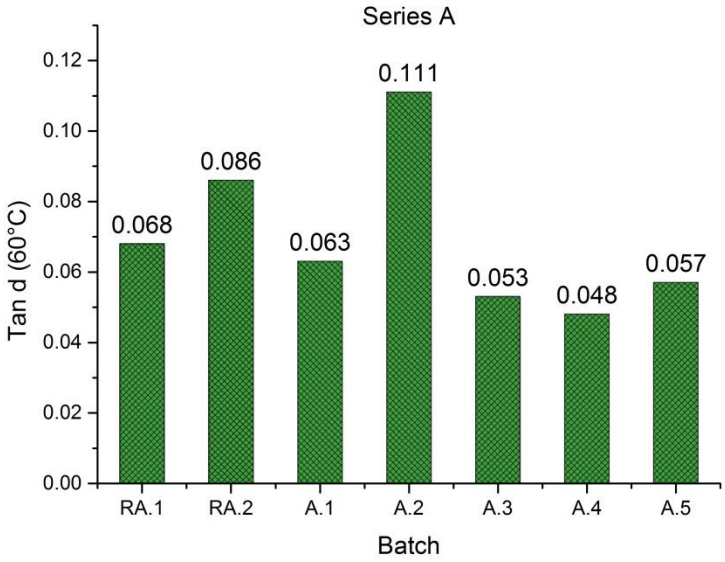

Figure 43. *Values of tan δ at 60°C for compounds in series A.*

Rolling resistance values are presented in Figure 43 and as it can be observed, compounds A.3, A.4 and A.5 present the best rolling resistance values. As expected, batches *RA.2* and A.2 show the poorest values of rolling resistance since the absence of silane and larger surface area affects negatively to the filler dispersion by increasing the fillers interparticle forces. Table 9 lists the values of tan δ (0°C), tan δ (60°C) and the ratio (0°C /60°C), which is very useful for the design of a tyre.

Table 9. *Dynamic mechanical properties of batches in series A.*

Batch	Tan δ (0°C)	Tan δ (60°C)	Ratio (0°C /60°C)
RA.1	0.165	0.068	2.426
RA.2	0.192	0.086	2.232
A.1	0.167	0.063	2.651
A.2	0.187	0.111	1.684
A.3	0.175	0.053	3.302
A.4	0.197	0.048	4.104
A.5	0.163	0.057	2.859

Analyzing this table it can be concluded that batches A.3, A.4 and A.5 are the batches that showed improvement in 0°C /60°C ratio, indicating an enhanced balance between two of the most important parameters in tyre industry: rolling resistance and wet grip. Batch A.4 shows a very good level of wet traction and excellent rolling resistance, while batch A.3 and A.5 show reasonable levels of wet traction and very good rolling resistance indicating good filler dispersion in the rubber matrix. However, as expected, batches with absence of silane and with larger surface area silica (*RA.2* and A.2) presented increased wet grip but poor rolling resistance due to the formation of filler-filler

networks. Batch A.1 presents similar results as *RA.1*, so the change on butadiene rubber type seems to have no effect on dynamic properties.

Table 10. *RPA results for compounds in series A.*

Batch	***R A.1***	***RA.2***	**A.1**	**A.2**	**A.3**	**A.4**	**A.5**
S* (dNm)	3.9	4.7	3.8	7.2	3.9	3.7	4.1
Tan δ (60°C) 0.2°	0.099	0.127	0.099	0.168	0.079	0.082	0.085

The values of rolling resistance were also measured with RPA and the results are presented in Table 10. As it can be seen, the results of rolling resistance with RPA are quite different as the measured with DMA, showing increased rolling resistance for all the batches. This difference in the measured values is most probably due to the different techniques and parameters used. DMA is a well contrasted method for measuring the dynamic properties, so based on previous experiences the results obtained with DMA are more trustworthy than those obtained with RPA.

7.1.2 Series B

As proceeded with Series A, the results of the conventional measurements of Series B are presented and discussed below and all the results are collected in Appendix 2.

Recipe & mixing

After analyzing results from series A, it was noticed that batch A.2 having a larger surface area silica, did not provide the expected results and the values of flocculation measurements, Payne effect, bound rubber and tensile properties were not satisfactory. For that reason, this series B is focused on the variation of some parameters from the original formulation of batch A.2 in order to detect how these variations affects to filler-polymer interactions. Therefore, in this series B the reference compounds are batch A.2 from series A and as in series A, batch A.2 without the addition of silane. A simplified version of the recipe and mixing program is presented in Table 11.

Table 11. *Recipe and mixing programs of compounds in Series B.*

Ingredient [phr]	***RB.1 (Batch A.2)***	***RB.2 (Batch A.2, no silane)***	**B.1**	**B.2**	**B.3**	**B.4**
NR + BR(Type I)	100	100	100	100	100	100
CB	10	10	10	10	10	10
Silica (Type II)	60	60	60	60	60	60
Silane (Type I)	5	-	5	5	8	5
DPG accelerator (Type I)	1	1	2	3	1	1
Rubber mastication	-	-	-	-	-	x
Mixing program 1	x	x	x	x	x	x
Mixing program 2	-	-	-	-	-	-

Mooney viscosity ML(1+4)

The results of Mooney viscosity for batches in series B are represented in Figure 44. As it can be observed, the value obtained for *RB.1* (Batch A.2) is in line with the value obtained for batch A.2 of series A. It is noticeable that similarly to series A, the batch *RB.2* without silane presents a huge increment in the value of Mooney viscosity. This may be attributed to the absence of silane coupling agent, what leads to an increment of filler-filler interactions and to a poor filler dispersion. Batches B.1 and B.2, with increased amount of DPG accelerator, showed the lowest Mooney viscosity values compared to the reference compound indicating that larger surface area silica requires increased amounts of DPG to reach a higher degree of silanization. Hence, filler dispersion is improved and the viscosity of the compound is reduced. Batch B.3, where the amount of silane coupling agent is increased showed a noticeable favorable viscosity value compared to the reference compound. Increased amount of silane increases the silanization rate since higher amount of ethoxy-silyl groups are available to react with silanol groups from silica surface. The reaction rate is increased till a plateau zone is reached due to limited amount of accessible silanol groups on silica surface. The use of masticated rubber within batch B.4 showed no significant variation of Mooney viscosity compared to the reference batch.

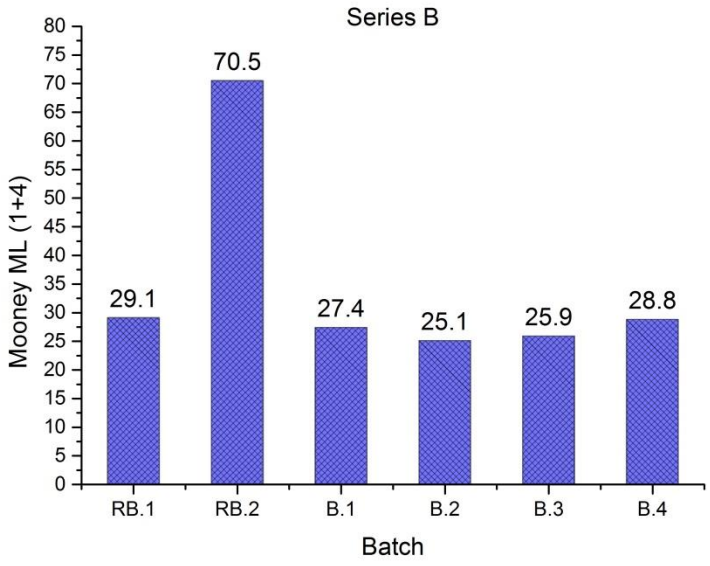

Figure 44. *Mooney viscosity values for batches in series B.*

DIN Abrasion

Figure 45 shows the results of the DIN abrasion test performed for compounds in series B. For batches *RB.2* and B.1 no results could be obtained due to some technical issues during measurements.

The effect of increased amounts of accelerator on abrasion resistance can be seen from batch B.2, where the values of abrasion resistance are slightly improved most likely due to increased filler-rubber interactions since silanes are performing more actively. The use of masticated rubber in batch B.4 provides slightly poorer values of abrasion resistance than the reference compound. The breakdown of natural rubber linkages during mastication leads to increased formation of filler-filler interactions deteriorating the abrasion resistance of the material.

The optimum value of abrasion resistance was obtained when the amount of silane coupling agent was increased in batch B.3. The improvement of abrasion resistance with increased silane contents is attributed to the contribution of increased released sulfur to the formation of chemical linkages within the rubber matrix. These chemical linkages suppress the mobility of the filler particles avoiding flocculation.

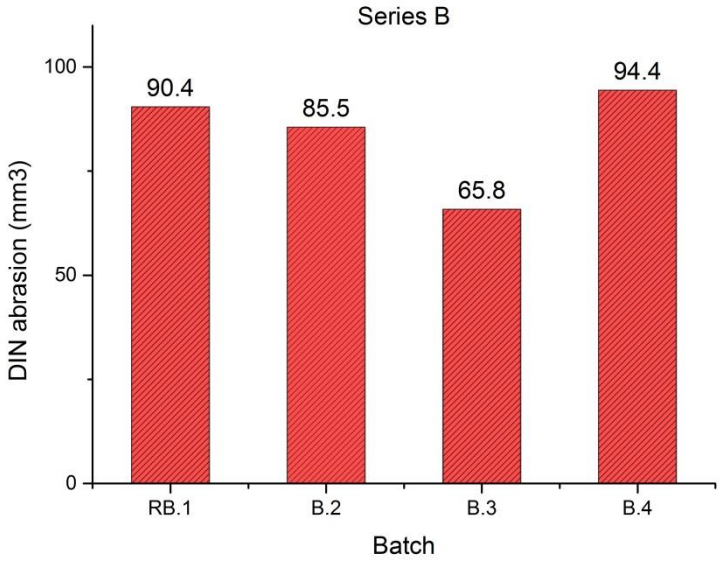

Figure 45. *DIN abrasion for batches in series B.*

Vulcanization characteristics

Table 12 presents the vulcanization characteristics of batches in series B. The obtained results of *t10* show different values for all the batches compared to compound *RB.1*. Values of *t90* of all the batches are also quite variable respect to the reference compound. This trend indicates that each compound offers different vulcanization character-

istics as result of the variations made to the original recipe of batch *RB.1*. In addition, it can be noticed that increased amount of silane (batch B.3) vastly increases both *t10* and *t90* values.

Table 12. *Vulcanization characteristics of compounds in series B.*

Batch	***RB.1***	***RB.2***	**B.1**	**B.2**	**B.3**	**B.4**
F_{min} (dNm)	1.5	5.6	1.3	1.2	1.3	1.5
F_{max} (dNm)	14.8	14.5	15.5	15.2	17.1	14.2
t10 (s)	2.7	3.8	3.9	3.1	4.8	2.9
t90 (s)	13.1	15.0	12.7	10.3	18.5	13.5

The values of F_{min} and F_{max} are quite similar for all batches except for batch *RB.2* that shows a huge increase in the value of minimum torque and lower values of maximum torque, thus referring to a minor stiffness of the material. However, the maximum difference between these values for batch B.3 indicates that increased silane concentration affects favorably to the stiffness of the material. Additionally, it can be noticed that larger amounts of accelerator slightly increase the stiffness of the compounds compared to the reference batch.

Dynamic properties: tan δ

The values of tan δ at 0°C for compounds in series B are presented in Figure 46. Values of wet grip are all in the same line of values as the reference compound indicating that none of the variations made to the original formulation of batch *RB.1* affects significantly to the wet grip values.

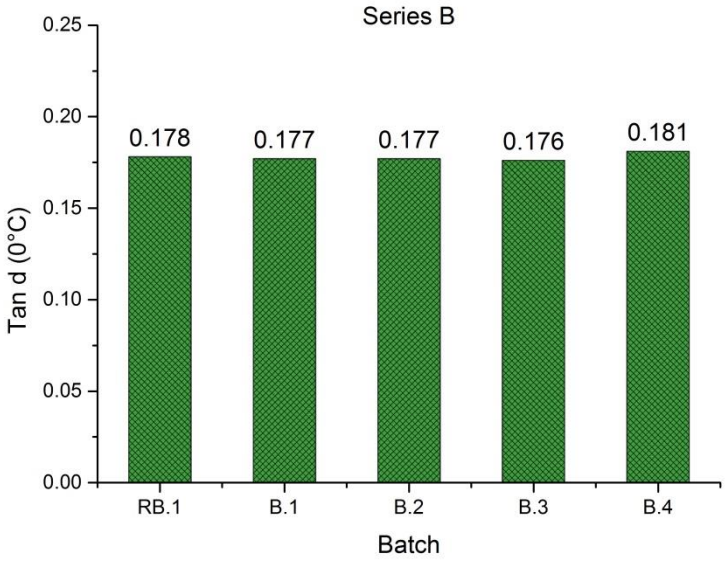

Figure 46. *Values of tan δ at 0°C for compounds in series B.*

Figure 47 presents the values of tan δ at 60°C for compounds in series B. As observed with values of wet grip, the values of tan δ at 60°C are also all in the same trend as the reference compound, showing a slight improvement for batch B.3 when the silane content is increased.

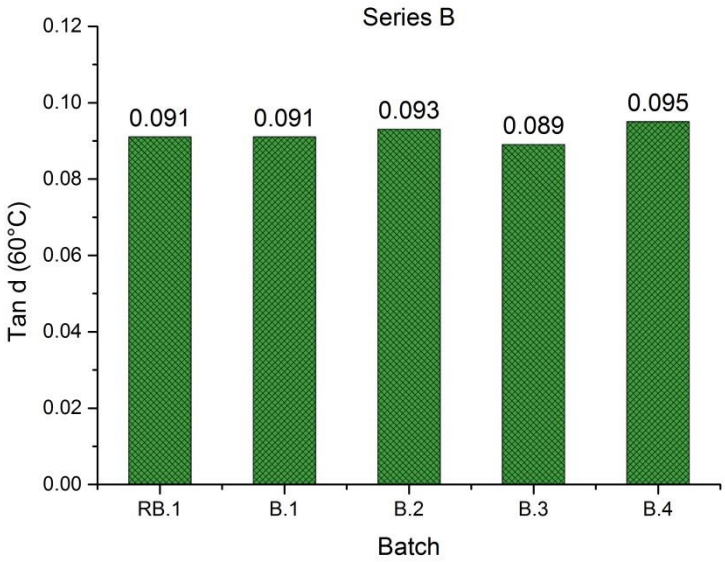

Figure 47. *Values of tan δ at 60°C for compounds in series B.*

Analyzing the ratios (0°C /60°C) presented in Table 13, it can be concluded that increased accelerator contents and the use of masticated rubber not affect significantly to the dynamic properties of batches in series B. However, it can be noticed that batch B.3,

with increased silane content, presents the most favorable 0/60 ratio showing improvement in both wet grip and rolling resistance properties. As explained before, this improvement may be attributed to a higher efficiency of the silanization reaction with increasing silane content during mixing.

Table 13. *Dynamic mechanical properties of batches in series A.*

Batch	Tan δ (0°C)	Tan δ (60°C)	Ratio (0°C /60°C)
RB.1	0.178	0.091	1.956
B.1	0.177	0.091	1.945
B.2	0.177	0.093	1.903
B.3	0.176	0.089	1.977
B.4	0.181	0.095	1.613

Similarly to series A and probably attributed to the same reasons, the rolling resistance values obtained from RPA greatly differs with the ones obtained from DMA. Based on experience the results from DMA are more accurate than those from RPA.

Table 14. *RPA results for compounds in series B.*

Batch	***RB.1***	***RB.2***	**B.1**	**B.2**	**B.3**	**B.4**
S* (dNm)	7.6	13.0	7.5	7.6	7.5	7.0
Tan δ (60°C) 0.2°	0.141	0.267	0.128	0.130	0.118	0.138

7.1.3 Series C

As proceeded with Series A and B, the results of the conventional measurements performed for batches in Series C are presented and discussed below and all the results are collected in Appendix 3.

Recipe & mixing

Series C is intended to study the effect of the variation of mixing times on filler-polymer interactions. For that purpose the mixing times of the batch *RC.1* (60 seconds each stage) were accordingly increased/decreased. Firstly, the mixing times of the two first segments of the mixing program were decreased from 60 seconds to 40 seconds in each segment. After that, the mixing times of these two segments were increased from 60 seconds to 80, 100, 120 and 140 seconds. A simplified version of the recipe and mixing program is presented in Table 15.

Table 15. *Series C recipe and mixing program.*

Ingredient [phr]	**C.1**	***RC.1* (Batch A.2)**	**C.2**	**C.3**	**C.4**	**C.5**
NR + BR(Type I)	100	100	100	100	100	100
CB	10	10	10	10	10	10
Silica (Type II)	60	60	60	60	60	60
Silane (Type I)	5	5	5	5	5	5
Accelerator (Type I)	1	1	1	1	1	1
Mixing program 1 (first 2 segments)	40 sec	60 sec	80 sec	100 sec	120 sec	140 sec
Mixing program 2	-	-	-	-	-	-

Mooney viscosity ML(1+4)

The effect of variable mixing times on Mooney viscosity can be observed in Figure 48. There is a clear trend of the values of Mooney viscosity with increased and decreased mixing times. As it can be seen, increased mixing times show lower values of Mooney viscosity while decreased mixing times show the opposite effect. These results were expected since when mixing times are extended higher degrees of rubber mastication are reached and the degree of filler dispersion is enhanced. Normally the degree of silanization reaction increases with time. Hence, under excessive mixing conditions the chains of the natural rubber are broken down leading to lower physical linkages in the compound corresponding to lower Mooney viscosities.

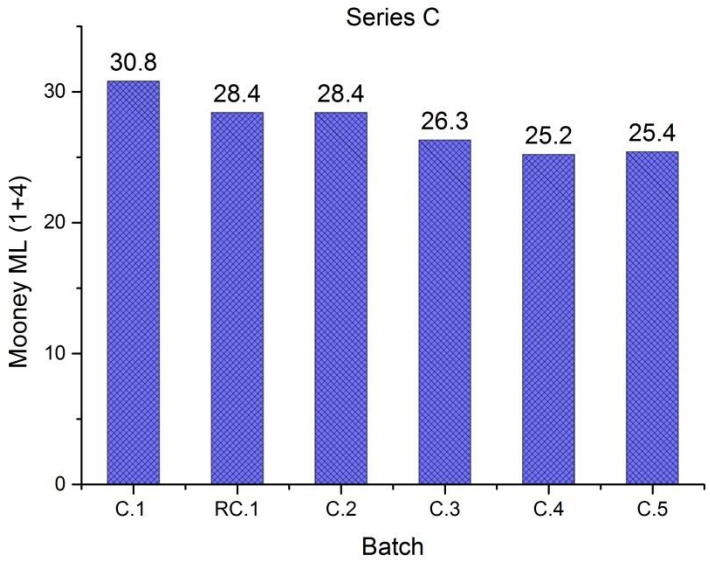

Figure 48. *Mooney viscosity values for batches in series C.*

DIN Abrasion

The results of DIN abrasion of compounds in series C are illustrated in Figure 49. According to this figure, variations on mixing times seem to have opposite effects on abrasion resistance than on Mooney viscosity. Shorter mixing times (batch C.1) shows the highest values of material loss compared to the reference compound. Apparently, a lower degree of silanization was reached due to shorter contact time between the components of the batch. As result, increased filler flocculation and lowered abrasion resistance was reached. Longer mixing times also shows adverse effect even though the material loss is reduced compared with the values obtained for compounds with shorter mixing times. This trend followed by the compounds in series C may be as a consequence of deteriorated material properties with excessive mixing times. The degree of silanization becomes higher with longer mixing times but simultaneously the optimum final properties of the material are reduced.

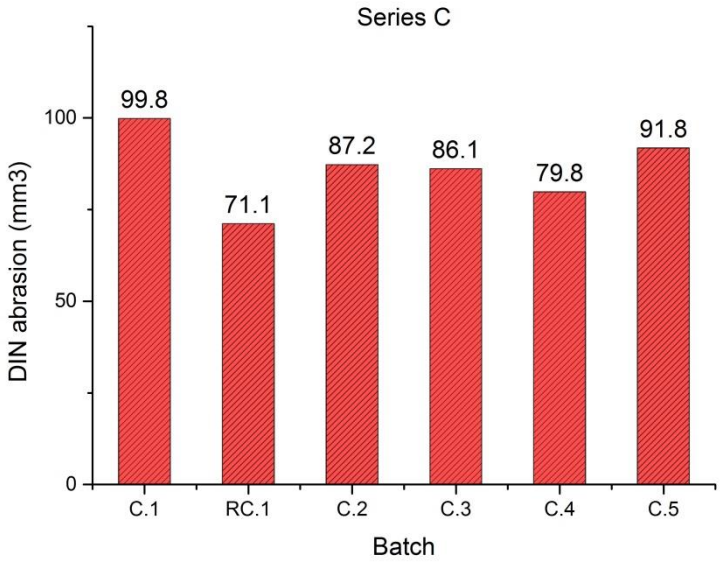

Figure 49. *DIN abrasion for batches in series C.*

Vulcanization characteristics

The vulcanization characteristics obtained for compounds in series C are listed in Table 16. According to these results, it is clear that increased mixing times also increase values of t10 and t90 and decreased mixing times show the opposite effect.

Table 16. *Vulcanization characteristics of compounds in series C.*

Batch	C.1	*RC.1*	C.2	C.3	C.4	C.5
F_{min} (dNm)	1.5	1.4	1.4	1.3	1.3	1.2
F_{max} (dNm)	14.4	14.7	14.4	13.8	13.5	13.5
t10 (s)	2.1	2.4	3.0	3.5	3.7	4.2
t90 (s)	13.3	13.4	14.2	14.3	14.1	14.4

The minimum and maximum torque values are quite similar for all the batches in series C. However, batch *RC.1* presents the highest difference between these values. Additionally, it can be noticed that longer mixing times tend to reduce the difference between maximum and minimum torque values compared to the reference batch. Thus, indicating that longer mixing times slightly decrease the stiffness of the compound. As commented before excessive mixing results in polymer chain scission, deteriorating the optimum final properties of the material.

Dynamic properties: tan δ

Figure 50 illustrates the values of tan δ at 0°C for compounds in series C. As it can be observed all the values are quite similar to the reference one indicating that variations of the mixing times do not affect significantly to the values of wet grip.

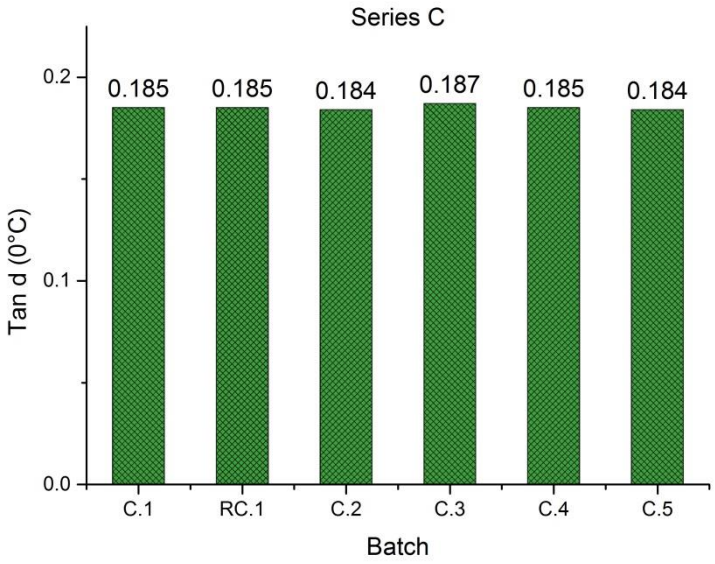

Figure 50. *Values of tan δ at 0°C for compounds in series C.*

Figure 51 shows the values of tan δ at 60°C for compounds in series C. It can be seen that the results are also in a similar line of values as the reference compound. However, batches C.3 and C.4 present a slight improvement on the values of tan δ at 60°C indicating that longer mixing times affect favorably to rolling resistance till a peak point is reached, at which the compound starts to lose their optimum properties.

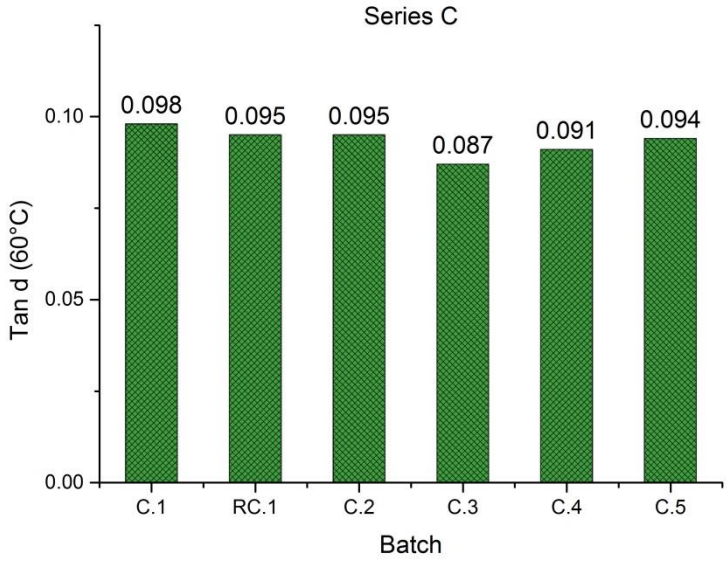

Figure 51. *Values of tan δ at 60°C for compounds in series C.*

Table 17 summarizes the values of 0/60 ratio and clearly batches C.3 and C.4 provides the optimum values of this ratio, showing good balance between wet traction and rolling resistance. This observation suggests that longer mixing times affect favorably the compromise between wet traction and rolling resistance. This trend might be attributed to the fact that longer mixing times results in higher degree of mastication of the polymer and a better filler dispersion on the rubber matrix. On the other hand, shorter mixing times affects negatively to this compromise increasing notably the values of rolling resistance.

Table 17. *Dynamic mechanical properties of batches in series A.*

Batch	Tan δ (0°C)	Tan δ (60°C)	Ratio (0°C /60°C)
C.1	0.185	0.098	1.887
RC.1	0.185	0.095	1.947
C.2	0.184	0.095	1.936
C.3	0.187	0.087	2.149
C.4	0.185	0.091	2.032
C.5	0.184	0.094	1.957

Similarly as in series A and series B, the rolling resistance values obtained from RPA greatly differs with the ones obtained from DMA as it is shown in Table 18, but as commented before DMA results are more accurate and reliable.

Table 18. *RPA results for compounds in series C.*

Batch	C.1	*RC.1*	C.2	C.3	C.4	C.5
S* (dNm)	7.5	7.5	7.1	6.8	6.3	6.3
Tan δ (60°C) 0.2°	0.151	0.149	0.147	0.145	0.144	0.139

7.2 Results of testing conducted to assess filler-polymer interactions

7.2.1 Bound rubber test

As described in the theoretical part, the bound rubber layers attached to the surface of silica filler can be both tightly and loosely bound rubber layers. In this study, the total bound rubber content is measured and the results are presented in Table 19.

Table 19. *Total bound rubber content of silica filled rubber in every mixing series.*

Series A		Series B		Series C	
Batch	**Bound rubber content (%)**	**Batch**	**Bound rubber content (%)**	**Batch**	**Bound rubber content (%)**
RA.1	54.04	*RB.1*	51.35	C.1	53.10
RA.2	50.04	*RB.2*	49.12	*RC.1*	54.96
A.1	52.88	B.1	50.79	C.2	50.96
A.2	59.92	B.2	50.91	C.3	51.81
A.3	52.34	B.3	49.50	C.4	50.12
A.4	53.84	B.4	51.20	C.5	50.93
A.5	56.87	-	-	-	-

Series A

Figure 52 represents the amounts of total bound rubber contents of batches in series A. As it can be observed, it is clear that batch A.2 shows the maximum amount of rubber attached to fillers surface in comparison with the batch *RA.1*. This increment is attributed to the highly active surface area resulting from the larger surface area silica used within this batch. Even though highly active surface area of silica provides greater filler-polymer interactions, the interparticles forces also become stronger facilitating filler agglomeration during mixing and storage.

As expected, batch *RA.2* presented the lowest amount of bound rubber since no silane coupling agent was added to the recipe and hence, no silanization reaction occurred. From this compound it is possible to evaluate the important influence of silane on bound rubber formation. It is clearly observed that silane coupling agents reduces the polarity differences between rubber and silica suppressing silica flocculation.

Batch A.5, where the DPG accelerator was added along with the curatives instead of incorporating it to the rubber during mixing, presents a favorable effect on the formation of bound rubber. It seems that the silanization reaction becomes more efficient when the accelerator is added along with the curatives. The main reason may be that when DPG is added during mixing, it is adsorbed by silica particles reducing the efficiency of the silanization reaction. However, the addition of DPG after mixing along with the curatives leads to increased degrees of silanization avoiding adsorption into the silica surface. Batches A.3 and A.4, formulated with silane type II show a poorer bound rubber formation compared with batch *RA*.1 evidencing that the use of silane type II affects negatively to filler-rubber interactions. Lastly, in batch A.1 it is remarkable that no favorable effects were noticed when using a functionalized butadiene rubber (type II).

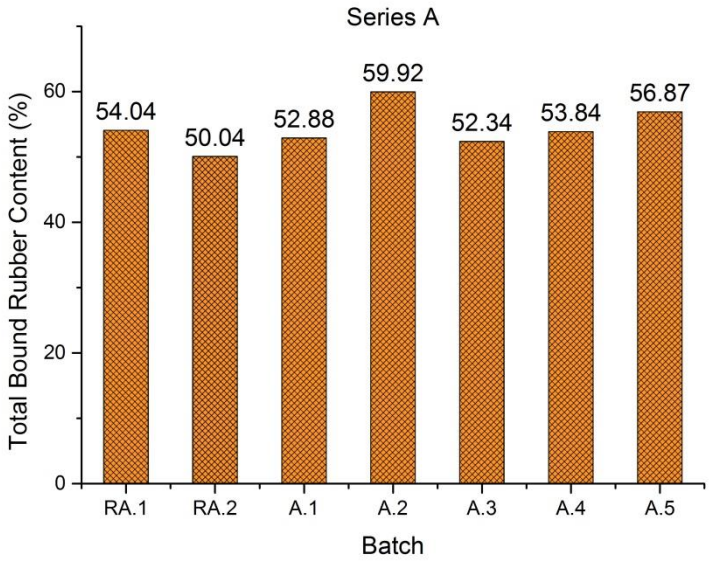

Figure 52. *Bound rubber content of batches in Series A.*

Series B

Figure 53 presents the bound rubber contents for batches in series B. According to this figure, the bound rubber values show little variations with the modifications made to the recipe of compound *RB.1*. As it can be noticed only increased silane contents (batch B.3) showed a slight increase in the bound rubber content. This improvement on bound rubber formation might be due to the fact that higher silane contents lead to higher degree of reaction between silane and OH groups present on silica surface, thus reaching increased filler-polymer interactions.

From batch *RB.2* it can be observed the influence of silane on bound rubber formation. As happened with series A, the bound rubber contents are greatly reduced with absence of silane coupling agents. The polarity mismatching between rubber and silica results in higher degrees of flocculation and reduced filler-polymer interactions.
Increased accelerator contents (batch B.1 and B.2) as well as the used of masticated rubber (batch B.4) do not show any improvement on bound rubber formation. These variations made to the original recipe of the reference compound seem not to affect greatly to the bound rubber values.

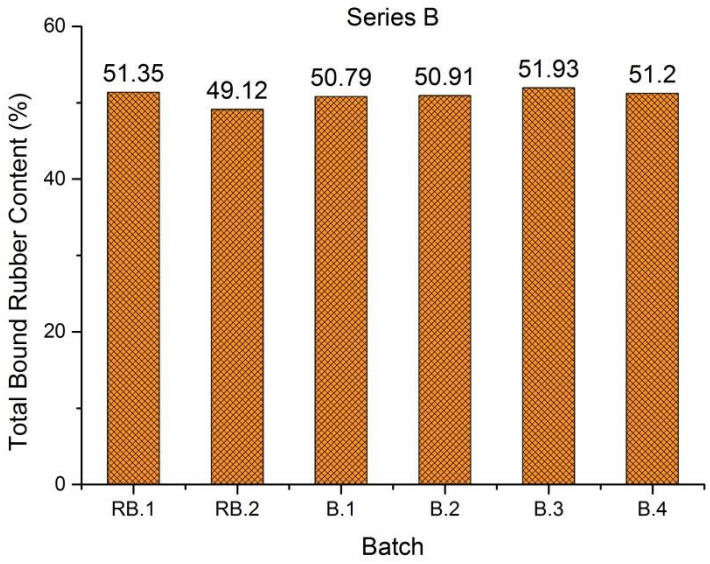

Figure 53. *Bound rubber content of batches in Series B.*

Series C

The bound rubber values obtained for batches in series C are illustrated in Figure 54. As it is shown, batch *RC.1* contains the highest values of bound rubber, evidencing that changes on mixing times have no favorable effects on bound rubber formation.
It is clear the trend followed by compounds in series C, lower bound rubber formation with longer mixing times. Basically, the reason for this lower bound rubber formation is the degradation of natural rubber with excessive shearing action. During excessive mixing, the reactive double bonds of natural rubber are destroyed leading to lower physical linkages between filler and rubber even though the degree of filler dispersion reached is higher. The molecular weight of the NR molecules is lower after mixing so the amount of bound rubber formed is reduced. An optimum mixing time must be encountered in order to promote as much bound rubber as possible. In this case, batch *RC.1* presents the optimum mixing time for bound rubber formation.

On the other hand, it is noticeable that shorter mixing times (batch C.1) also reduces bound rubber formation. Too short mixing results in lower degrees of silanization and reduced filler-polymer interactions.

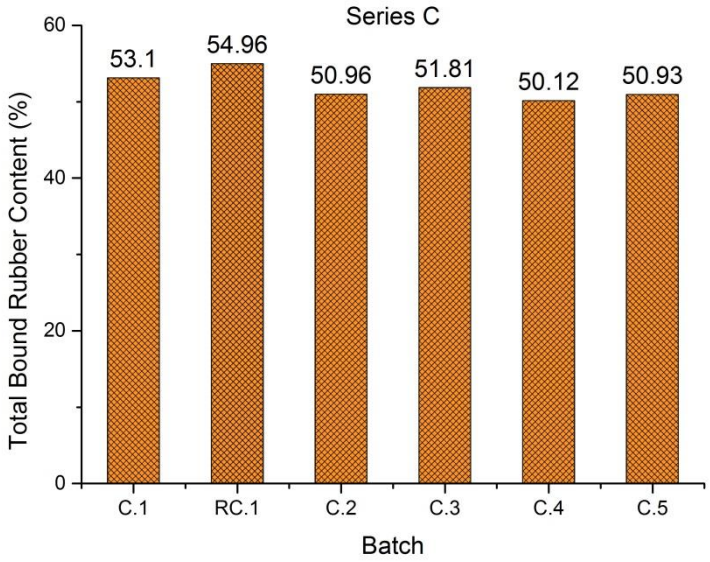

Figure 54. *Bound rubber content of batches in Series C.*

7.2.1.1 Effect of bound rubber on silica flocculation

The assessment of bound rubber formation is very important to evaluate the degree of filler-polymer interactions, which plays an important role in silica flocculation. As indicated before, silica tends to self-associate within the rubber matrix due to polarity differences. The addition of silane coupling agent drastically reduces silica flocculation rates through silanization reaction. It is important to mention that bound rubber test is not a very accurate technique and many differences in the results can be found within each different measurement. Nevertheless, it is a good method to have an approximation of the magnitude of filler-rubber interactions.

According to the results obtained from this measurement, it is possible to notice that the absence of silane coupling agents strongly reduces filler-polymer interactions leading to poor silica dispersion. Moreover, the results of series A indicates that larger surface area silica notably increases the bound rubber formation due to higher interactions between silane and OH groups present on silica surface and the addition of the DPG accelerator with the curatives also affects favorably to the formation of bound rubber. Variations made to compounds in series B do not present important effects on bound rubber formation and just the increase of silane coupling agent contents shows a

slight improvement on the filler- polymer interactions. From the results obtained in series C, it can be concluded that variations in the mixing times present adverse results on bound rubber formation. Excessive mixing leads to lower physical linkages on the rubber matrix due to the breakdown of the reactive double bonds of natural rubber chains and shorter mixing time results in an ineffective silanization reaction. Therefore, filler-rubber interactions are reduced resulting in lower contents of bound rubber and increased filler networks formation.

7.2.2 Tensile properties

As mentioned in previous chapters, the reinforcing effect of filler particles refers to their capability to enhance mechanical properties, such as tensile strength and reinforcing index (M300/M100). Measuring the tensile properties of vulcanizates provides useful information about the filler dispersion on the rubber matrix and thus, it is possible to assess the extent of filler-polymer interactions.

The filler-filler networking formed within silica particles during flocculation are broken at approximately 10% of deformation. Consequently, the reinforcing index (M300/M100) gives information about the reinforcing effect of filler particles at large deformations. In addition, M300/M100 ratio is commonly used as an indication of the rolling resistance of a tyre, referring to the tensile curve shape. It is generally known that M300/M100 index may show a relationship between tan δ at 60°C and bound rubber content. The thickness of the bound rubber layer formed on the silica surface plays an important role on their reinforcing properties and thus, on the M300/M100 ratio.
The results of tensile properties measurements for each mixing series are presented and discussed below.

Series A

In Table 20 the results of the measured tensile properties of compounds in series A are listed, including stress at break (MPa), elongation at break (%), stress at 100% strain (M100), and stress at 300% strain (M300).

Table 20. *Tensile properties of batches in series A.*

Batch	Stress at break (MPa)	Elongation at break (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	M300/M100
RA.1	17.47	651.54	1.15	5.68	4.94
RA.2	-	-	-	-	-
A.1	16.71	635.59	1.10	5.47	4.97
A.2	18.90	838.06	1.08	4.61	4.27
A.3	15.41	491.18	0.97	4.33	4.46
A.4	14.31	540.00	1.24	5.92	4.77
A.5	15.75	548.47	1.36	6.86	5.04

Mechanical properties of the compounds such as tensile strength and reinforcing index are parameters directly influenced by filler-filler networks formed during silica flocculation. These mechanical properties of the compounds in series A are shown in Figure 55. Analyzing the obtained results and in the same trend as previous measurements, the addition of DPG accelerator along with the curatives (batch A.5) provided the optimum tensile properties. The silane coupling agent performs more efficiently providing a higher degree of silanization, what results in a better filler dispersion and improved reinforcing index. As a consequence, the material becomes harder and the elongation at break and stress at break are reduced. Filler-filler interactions are reduced and less energy loss is involved in the breakdown of the filler networks.

The use of a functionalized butadiene rubber (batch A.1) shows a slight improvement on the reinforcing index compared with the reference compound. This improvement along with the reduction of stress and elongation at break evidences the better mechanical properties exhibited by batch A.1, resulting from increased filler-rubber interactions between the rubber matrix.

As expected, the poorest reinforcing index and highest stress and elongation at break observed in batch A.2 were attributed to the large particle size of the silica filler. Reduced particles size was found to improve the mechanical properties of the compounds, while large particle size fillers strongly tend to self-associate forming aggregates, which affect negatively to the final mechanical properties of the material. Moreover, higher amount of energy is associated to the breakdown of the filler network. Since batch A.2 provides the most adverse results it is taken as the reference compound for further mixing series.

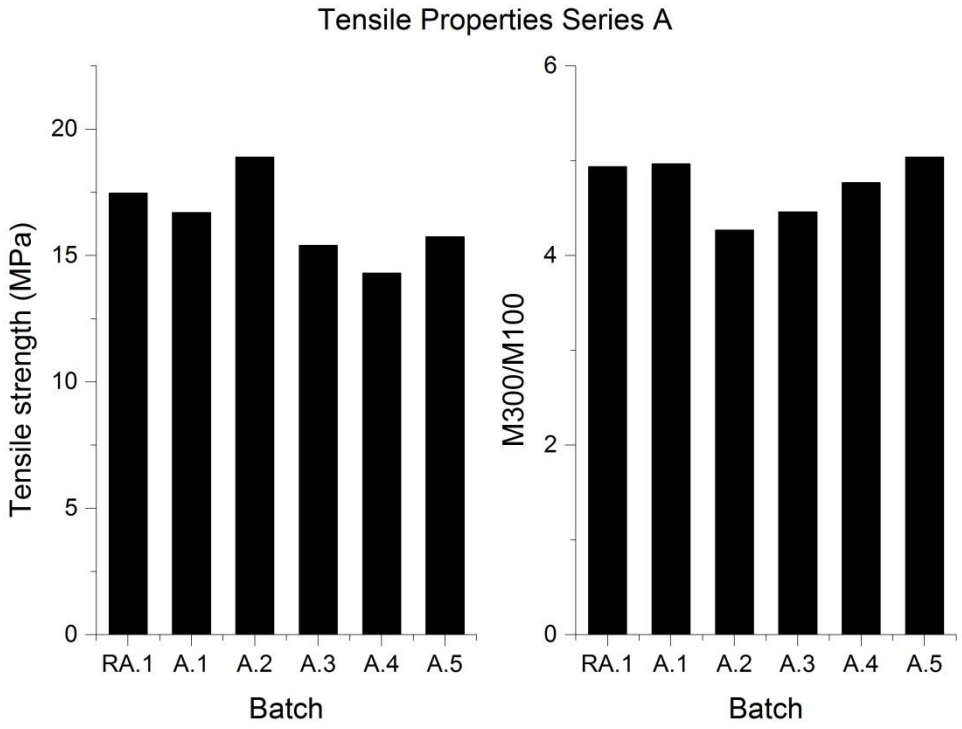

Figure 55. *Tensile properties for compounds in series A. Tensile strength and reinforcing index (M300/M100).*

The influence of the type of silane coupling agent on mechanical properties can be observed in batches A.3 and A.4. Comparing these batches with the reference compound, it is clear that the use of silane type II shows and adverse effect towards the reinforcing index. However, stress at break and elongation at break are also diminished providing contradictory results. This contradiction may be due to excessive curing or a reduced activity of the silane. Additionally, the reduction of silane activity leads to a reduced degree of silanization and hence, to poorer filler dispersion resulting in poorer mechanical properties.

Series B

In Table 21 the results of the measured tensile properties of compounds in series B are listed, including stress at break (MPa), elongation at break (%), stress at 100% strain (M100), and stress at 300% strain (M300).

Table 21. *Tensile properties of batches in series B.*

Batch	Stress at break (MPa)	Elongation at break (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	M300/M100
RB.1	18.46	530.65	1.37	4.71	3.43
RB.2	11.21	638.85	0.67	2.39	3.56
B.1	17.75	680.54	1.32	5.84	4.42
B.2	17.65	576.52	1.58	7.49	4.74
B.3	18.31	653.32	1.48	6.50	4.39
B.4	17.68	474.82	1.88	9.58	5.09

Figure 56 represents the tensile strength and reinforcing index for batches in series B. As mentioned before, the reference compound in series B (*RB.1*) contains larger surface area silica and variations were made to its original recipe in order to improve the previously showed adverse behavior. The influence of increased amounts of accelerator on the tensile properties can be observed comparing the results of batches B.1 and B.2 with the reference compound. As expected, increased amounts of accelerator provides higher reinforcing indexes and improved stress at break and elongation at break. Increasing the amount of DPG accelerator increases the degree of silanization stimulating filler-rubber interactions. Stronger interactions between rubber and fillers results in reduced filler agglomeration and better filler dispersion within the rubber matrix.

The effect of the absence of silane on tensile properties are shown by batch Reference B.2, where high amounts of filler networks are formed due to polarity differences between the rubber and silica fillers. The mechanical properties of this batch could not be measured properly since the material showed a very adverse behavior.

Regarding to the influence of silane coupling agent contents (batch B.3), increased amount of silane leads to an improvement on the reinforcing index, however, stress at break and elongation at break do not behave favorably. Pre-crosslinking during mixing may be the cause of this behavior leading to higher filler flocculation and adverse effects on the ultimate tensile properties.

Lastly, the influence of masticated rubber on the tensile properties can be observed on batch B.4. This batch presents the optimum reinforcing index as well as the minimum stress at break and elongation at break. The reason for this might be that lower rubber viscosity allows better filler dispersion and thus, the properties of the final compound are improved. Despite these favorable results, previous measurements do not showed significant effects when masticated rubber was used.

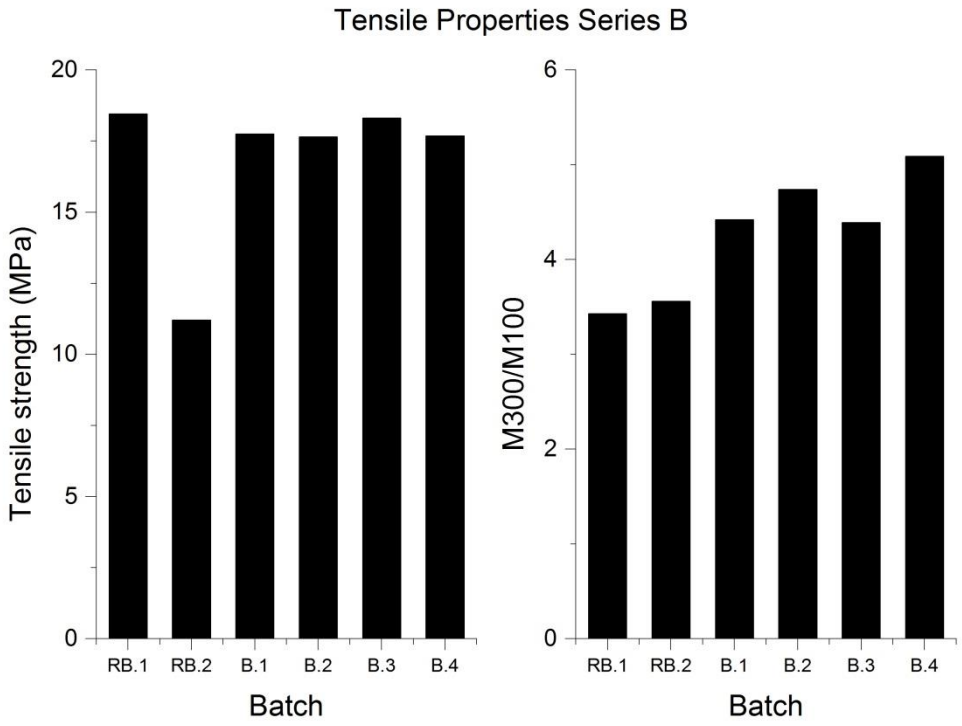

Figure 56. *Tensile properties for compounds in series B. Tensile strength and reinforcing index (M300/M100).*

Series C

In Table 22 the results of the measured tensile properties of compounds in series C are listed, including stress at break (MPa), elongation at break (%), stress at 100% strain (M100), and stress at 300% strain (M300).

Table 22. *Tensile properties of batches in series C.*

Batch	Stress at break (MPa)	Elongation at break (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	M300/M100
C.1	17.97	708.04	1.25	5.40	4.32
RC.1	18.13	698.05	1.29	5.62	4.35
C.2	17.96	676.37	1.28	5.81	4.54
C.3	17.42	667.93	1.25	5.68	4.54
C.4	17.07	538.15	1.52	7.68	5.05
C.5	17.41	483.76	1.75	9.07	5.18

From Figure 57, the influence of the mixing extension on tensile properties of the compounds in series C can be observed. As expected, shorter mixing times (batch C.1) leads to lower reinforcing index and worse ultimate tensile properties. This observation sug-

gests insufficient mixing times in batch C.1 resulting in stronger filler-filler interactions and poor dispersion. This batch presents the most adverse mechanical properties since with shorter mixing times there is not enough shear action to break down the filler agglomerates formed due to filler-filler interactions.
On the other hand, longer mixing times (batches C.2, C.3, C.4 and C.5) shows opposite behaviors of the compounds regarding tensile properties. When comparing those compounds with batch *RC.1*, it is clear that the reinforcing index is higher while stress at break and elongation at break are lower with increasing mixing times. This trend is reasonable since higher filler-polymer interactions take place reducing filler flocculation, thus, the final mechanical properties of the compounds are maximized till a an optimum point is reached. Excessive shearing action leads to degradation of rubber chains resulting in deteriorated mechanical properties.

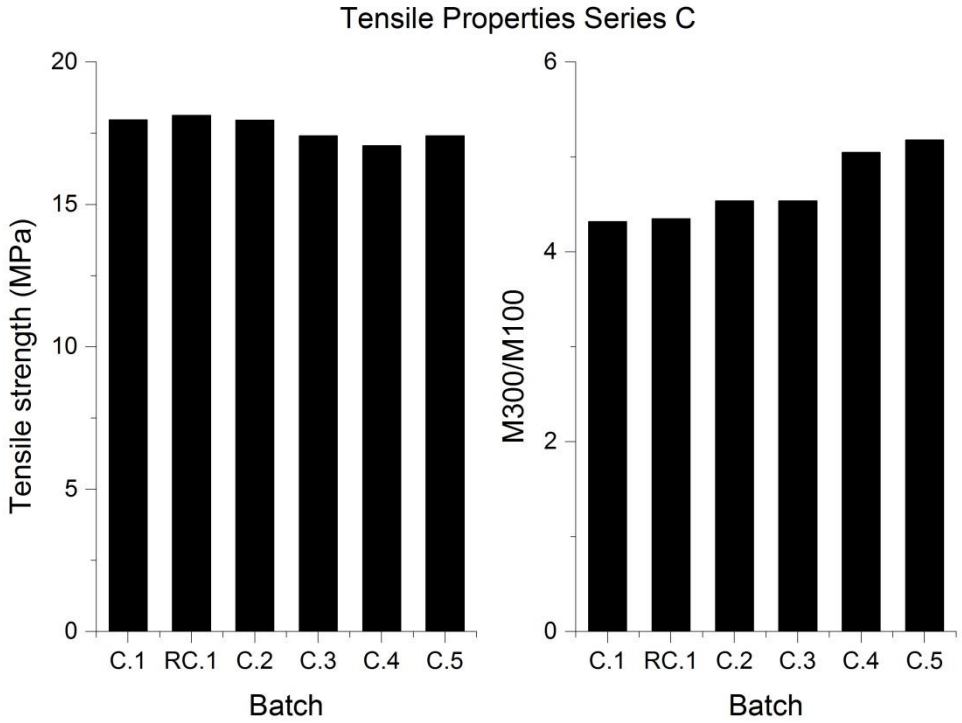

Figure 57. *Tensile properties for compounds in series C. Tensile strength and reinforcing index (M300/M100).*

7.2.3 Flocculation studies

7.2.3.1 Measurement of the curing curves

As previously documented in the literature part, the curing curves of silica-filled rubbers are divided into two different regions. The first region normally represents an increase in torque values at the beginning of vulcanization indicating silica flocculation due to

the strong tendency of fillers to self-associate. The higher the values of this increment the stronger the filler-filler interactions and consequently, poorer filler dispersion within the rubber matrix.
In addition to the network structures formed during vulcanization, such as filler-rubber and rubber-rubber linkages, it might be considered that filler-filler interactions also contributes to the final torque values reached within the rheometer curve.
In this section, the curing curves of the compounds of each mixing series are presented and the increment in torque values at the initial phase of vulcanization is evaluated in order to estimate the degree of filler flocculation, which plays an important role on the final properties of the material.

Series A

Figure 58 shows the rheometer curves of the compounds in series A. Based on this figure, it is possible to evaluate how the variations made to the reference recipe affects to silica flocculation within the rubber matrix giving an approximation of the extent of filler particles re-agglomeration. The individual curing curves of each compound in series A are presented in Appendix 4.

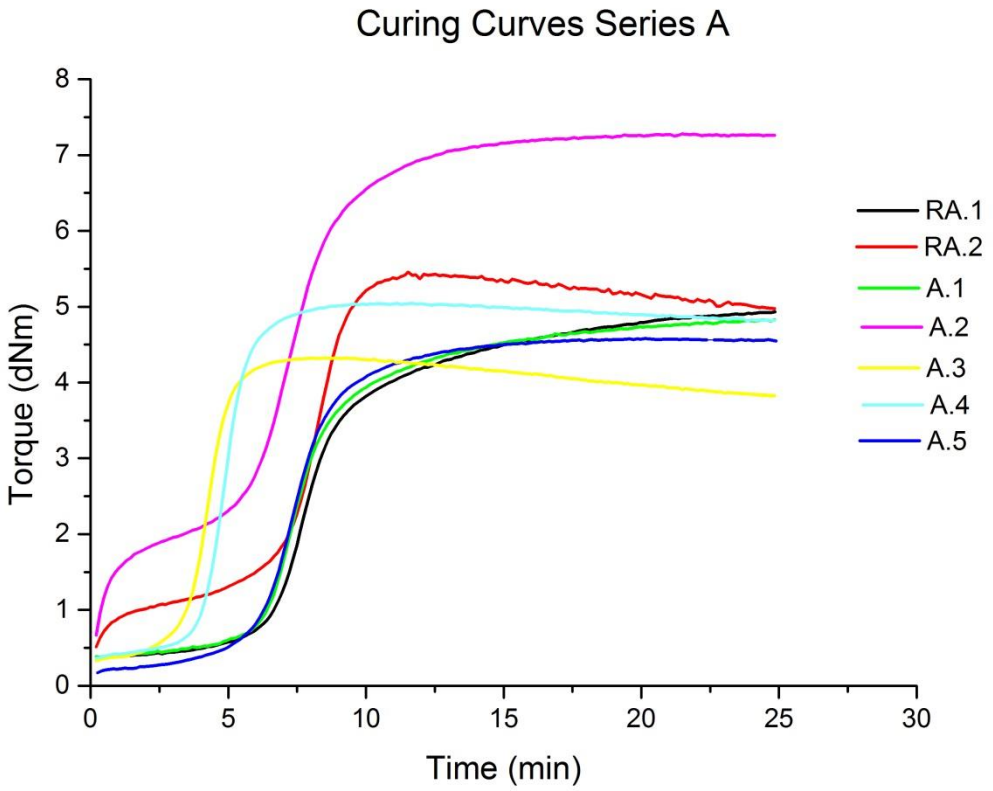

Figure 58. *Curing curves for compounds in series A.*

As it can be observed, compound *RA.1* presents an expected cure curve without a significant increase of the torque values at the beginning of vulcanization indicating absence of flocculation. The absence of silane coupling agent in batch *RA.2* leads to an inadequate reversing cure curve with high degree of flocculation due to filler particles reagglomeration. No silanization reaction takes place and the polarity differences between the rubber and the silica filler results in strong filler interactions and poor filler dispersion.

When comparing the rest of the samples with compound *RA.1* it can be noticed that batch A.5 presents the optimum curing curve with no flocculation and reaching a plateau zone at the end of vulcanization. It seems that when DPG accelerator is added with the curing package it performs in a more active way. This may be attributed to the fact that when DPG is added during mixing it is partially adsorbed into the silica surface and its performance is notably reduced. However, when added along with the curatives the degree of silanization is higher and improved silica dispersion is reached. This favorable result of batch A.5 follows the same trend than the results obtained from previous measurements.

Batch A.4 also presents an adequate cure curve without flocculation and decent final torque values, so that the combination of accelerator type II and silane type II used within this recipe reduces significantly filler-filler interactions providing good filler dispersion.

Batch A.1 shows quite similar results as the reference compound, so that type II of butadiene rubber used has no significant effect on filler flocculation. However, the use of silane type II in batch A.3 shows low flocculation rates but an adverse reversing cure curve most likely due to inappropriate silane activity.

When studying large surface area silicas, as in the case of batch A.2, it is possible to detect the maximum increase in torque values at the initial phase of vulcanization. This increment is taken as a clear evidence of silica flocculation, what is fairly reasonable since highly active silica surface area results in stronger filler-filler interactions and faster flocculation rates. It also can be noticed that batch A.2 shows the higher rheometer maximum torque as a result of filler aggregates contribution. Due to the fact that batch A.2 gives the most adverse results on silica flocculation, following series B and C are focused on making some variations its original recipe intended to reduce filler-filler networking and enhance the final properties of the compound.

Series B

The previously discussed results of series A indicated that batch A.2 showed the highest flocculation rates. This series B takes this batch A.2 as the reference compound (*RB.1*) and variations are made to its formulation in order to reduce flocculation. The resulted cure curves of compounds in series B are presented in Figure 59. The individual curing curves of each compound in series B are presented in Appendix 5.

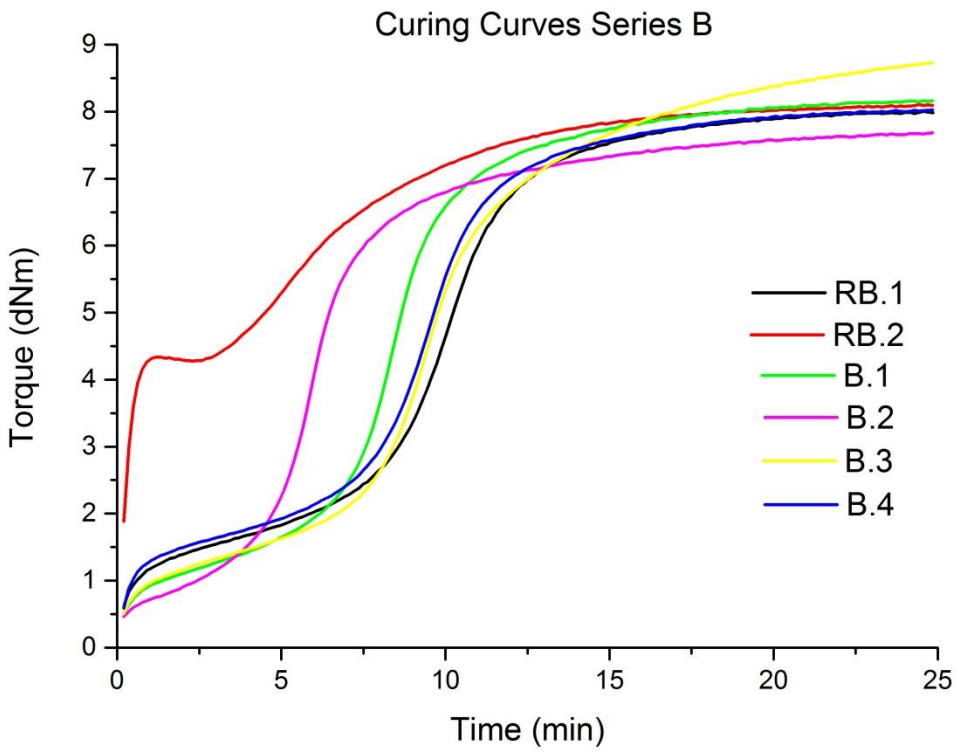

Figure 59. *Curing curves for compounds in series B.*

Comparing the curing curves of batches in series B with batch *RB.1*, it can be noticed that batches B.1, B.2 and B.3 slightly reduces filler flocculation. The influence of silane on filler flocculation can be observed in batch *RB.2*. As expected, the absence of silane coupling agent shows undesirable results since no silanization reaction takes place and filler particles strongly tend to self-associate. However, batch B.4 seems to show quite similar results than batch reference B.1 indicating that the use of masticated rubber has no remarkably influences on filler flocculation.

The effect of increased amounts of accelerator (batches B.1 and B.2) slightly reduces the degrees of filler-filler interactions as well as the maximum torque values of the cure curve, also indicating a reduced extent of filler-filler interactions. The activity of silane coupling agents is improved with increased accelerator contents.

Increased silane coupling agent content (batch B.3) shows slightly decreased extent of silica flocculation, however, the cure curve shows a marching trend probably due to increased filler-rubber interactions.

The use of masticated rubber in batch B.4 presents similar results than the reference compound, thus indicating that this variation has no significant influences on filler flocculation.

Series C

Figure 60 illustrates the cure curves obtained for the batches in series C, in which the mixing times are increased/decreased with respect to the batch *RC.1*. The individual curing curves of each compound in series C are presented in Appendix 6.

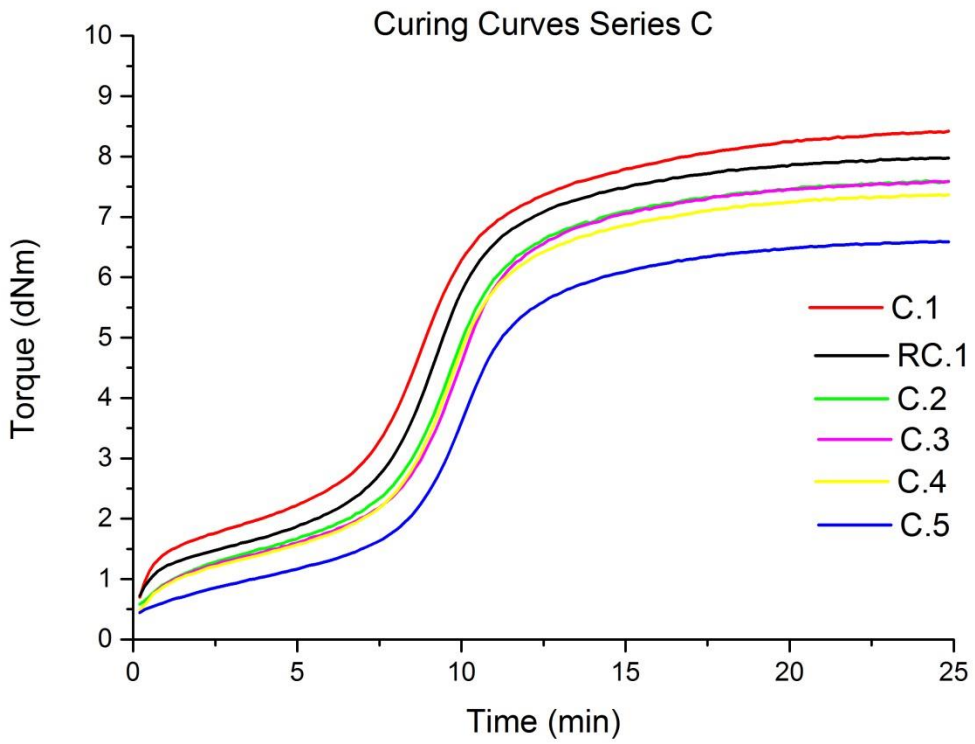

Figure 60. *Curing curves for compounds in series C.*

The influence of the mixing extension on filler flocculation can be observed from the curing curves illustrated in Figure 60. From the initial increment of torque within curing curve of batch C.1 it can be concluded that shorter mixing times provides increased filler flocculation compared to batch *RC.1*.

On the other hand, the curing curves of the batches with increased mixing times (batches C.2, C.3, C.4 and C.5) reveal that flocculation is reduced with extended shearing action. Filler aggregates are broken down and enhanced filler dispersion on the rubber matrix is reached. These results are in accordance to previously presented results. After an optimum mixing time is reached, mechanical properties of rubber compounds start to deteriorate.

7.2.3.2 Measurement of the kinetics of silica flocculation

As explained before, it is possible to study the mobility of the silica particles of uncured rubber compounds without curatives at elevated temperatures. For that reason, the increment of storage modulus at low strain amplitudes was monitored at temperatures ranging from 100°C to 140°C and taken as evidence of silica flocculation. The calculated flocculation rate constants refer to how fast the silica particles form aggregates under different thermal conditions. Low values of k_a indicate slower flocculation or low tendency of silica particles to self-associate within the rubber matrix during storage or thermal treatments. Normally, flocculation develops faster with increased temperature since the particles are able to move faster forming filler-filler networks. The flocculation rate constants were calculated for each compound at different temperature ranges and the results are presented and discussed below.

Series A

Table 23. *Flocculation rates of batches in series A at different temperatures.*

	Temperature (°C)	***RA.1***	***RA.2***	**A.1**	**A.2**	**A.3**	**A.4**	**A.5**
k_a (min^{-1})	100	0.228	0.305	0.225	0.292	0.230	0.218	0.182
	110	0.230	0.327	0.227	0.314	0.234	0.222	0.186
	120	0.233	0.330	0.231	0.318	0.239	0.229	0.191
	130	0.235	0.366	0.232	0.327	0.242	0.231	0.199
	140	0.241	0.375	0.239	0.333	0.249	0.239	0.211

Analyzing the values obtained for the flocculation rate constants presented in Table 23, it can be noticed that the results follow the same trend as the results obtained from the cure curves in previous section. Increased values of flocculation rate constant k_a means faster aggregates formation and poorer particles dispersion. Based on that and comparing all batches with batch *RA.1*, it was found that batch A.5 presents the slowest flocculation development, supporting in this way the results obtained from the curing curves and evidencing that the addition of DPG accelerator with the curing package improves notably filler-polymer interactions.

As expected, batch *RA.2* shows the fastest flocculation rates clearly due to the absence of silane coupling agents. Batch A.1, as in previous section, shows very similar flocculation rates constants as the reference batch indicating that the use of butadiene rubber type II does not affect significantly to filler-filler interactions.

Flocculation rates are highly influenced by silica surface area as evidenced in batch A.2. It is clear that larger surface area silica results in faster flocculation development. This phenomenon may be attributed to higher interparticles forces occurring when using highly active surface area silica.

The use of silane coupling agent type II (batch A.3) shows no great influences on flocculation rate constant. Finally, batch A.4 when silane type II and accelerator type II are used seems to present slower filler-filler network formation leading to improved filler dispersion within the rubber matrix.

From Table 23 it was also possible to notice that flocculation rate constant strongly depends on temperature. The mobility of silica particles is increased at higher temperatures and filler-filler interactions become stronger. The graphs illustrating silica flocculation development of compounds in series A at different temperatures are presented in Appendix 7.

Series B

Table 24. *Flocculation rates of batches in series B at different temperatures*.

	Temperature (°C)	***RB.1***	***RB.2***	**B.1**	**B.2**	**B.3**	**B.4**
k_a (min^{-1})	100	0.276	0.366	0.206	0.208	0.190	0.278
	110	0.281	0.448	0.207	0.210	0.198	0.280
	120	0.288	-	0.206	0.212	0.205	0.287
	130	0.296	0.522	0.231	0.227	0.211	0.294
	140	0.299	0.646	0.241	0.236	0.219	0.295

The flocculation rate constants of compounds in series B are listed in Table 24. As it can be seen, the increment of accelerator contents (batches B.1 and B.2) leads to slower flocculation rates most likely due to an improved activation of silanization reaction. As expected, the batch *RB.2* shows the fastest flocculation development due to the absence of silane.

Similarly to the results obtained from the cure curves, increased contents of silane coupling agent (batch B.3) favorably affects filler dispersion by reducing the flocculation rate constants. Apparently an increased degree of silanization is reached resulting in good filler dispersion. The use of masticated rubber in batch B.4 has no apparent consequences on flocculation rate constants, showing similar results as the reference compound.

Additionally, the same trend of increased flocculation rates with increasing temperatures can be observed. The graphs illustrating silica flocculation development within compounds in series B at different temperatures are presented in Appendix 8.

Series C

Table 25. *Flocculation rates of batches in series C at different temperatures.*

	Temperature (°C)	**C.1**	***RC.1***	**C.2**	**C.3**	**C.4**	**C.5**
$\mathbf{k_a}$ **($\mathbf{min^{-1}}$)**	100	0.255	0.246	0.213	0.215	0.207	0.201
	110	0.265	0.255	0.222	0.223	0.214	0.211
	120	0.271	0.261	0.226	0.229	0.222	0.218
	130	0.289	0.277	0.233	0.236	0.229	0.224
	140	0.293	0.281	0.239	0.238	0.234	0.230

The effect of increased/decreased mixing times on flocculation rate constants can be observed from Table 25. The results reveal that decreased mixing times (batch C.1) results in faster flocculation development compared with the reference compound, since the degree of silanization reached is notably decreased and filler particles tend to self-associate.

On the other hand, increased mixing times (batches C.2, C.3, C.4 and C.5) leads to lower flocculation rate constants. Longer shearing effect enhances filler dispersion by improving the degree of silanization and thus, increased filler-polymer linkages are formed. However, excessive shearing action might deteriorate the physical properties of the final compound.

As observed in previous series, temperature greatly affects to flocculation rates constants. Flocculation rate constants are increased at higher temperatures and faster filler-filler networks are formed. The graphs illustrating silica flocculation development of compounds in series C at different temperatures are presented in Appendix 9.

7.2.4 Payne effect measurements

Payne effect measurements were conducted intended to determine the degree of filler-polymer interactions occurring in silica filled rubber matrix. Besides, Payne effect plays an important role on the degree of reinforcement of silica filled rubbers, which is directly affected by filler-filler networks formation. The results of Payne effect measurements for each mixing series are presented and discussed below.

Series A

Figure 61 illustrates the resulting Payne effect for the compounds in series A. When analyzing these results and comparing all the batches with batch *RA.1*, it can be noticed that batch *RA.2* and batch A.2 show the maximum values of Payne effect. The effect of silane coupling agents on Payne effect can be observed from batch *RA.2*. Absence of

silane suppresses silanization reaction resulting in poor silica dispersion within the rubber matrix. Nonexistent silanization leads to increased formation of filler-filler aggregates showing higher difference in storage modulus with increasing strain amplitudes.

Larger surface area silica used in batch A.2 results in the highest values of Payne effect. The highly active surface area of silica leads to increased interparticle forces and hence, filler-filler interactions become stronger. As consequence the poor filler dispersion reached drastically reduces the reinforcing capacity of silica.

Comparing Batch A.1 with *RA.1* compound, an improvement in values of Payne effect can be noticed. It seems that the use of a functionalized butadiene rubber affects favorably to filler dispersion. However, contradictory results can be noticed when these results are associated with results obtained for previously conducted conventional measurements. This contradiction may be attributed to undesirable pre-crosslinking during mixing since NR can start its reaction with sulfur released from TESPT at a temperature about 120°C.

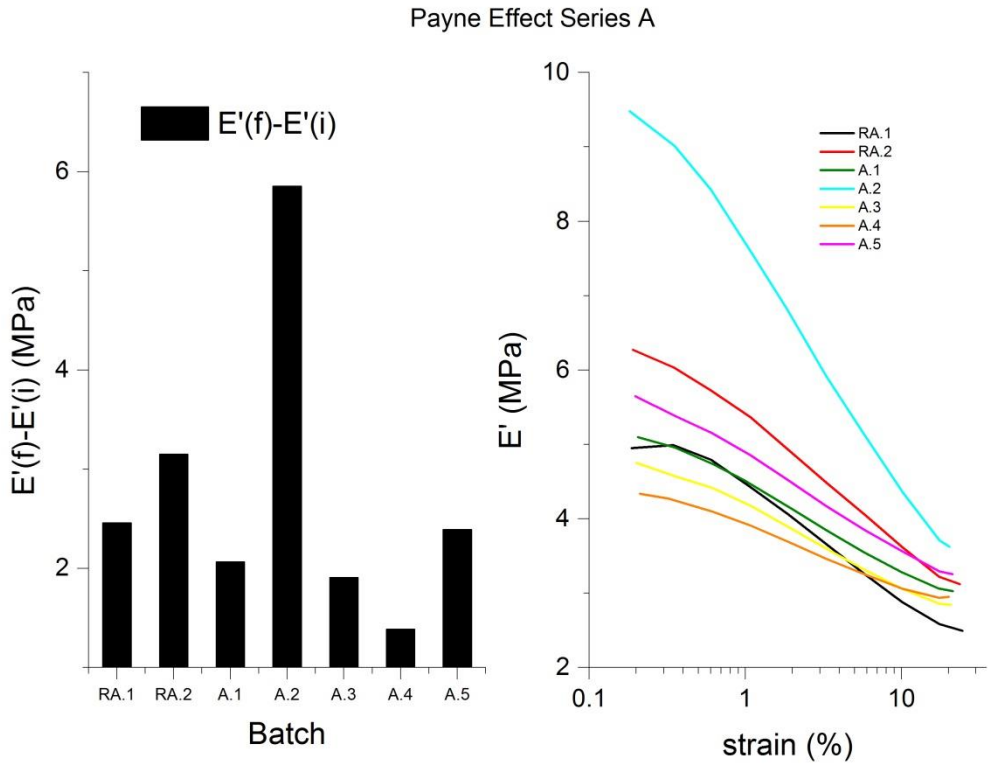

Figure 61. *Payne effect of batches in series A.*

Apparently, by using silane type II (batch A.3) the Payne effect value diminishes compared to the reference compound. As in the case of batch A.1, this result is contradictory with values obtained for the previously conducted measurements.

Payne effect is slightly improved when the DPG accelerator is added with the curing additives (batch A.5). Similarly to previous results, batch A.5 shows improved flocculation levels compared to the reference compound. As previously mentioned, the degree of silanization is increased within this batch and good filler dispersion is reached. The addition of DPG along with the curing package avoids its adsorption on silica surface improving notably its effect on silanization reaction.

The lowest difference of storage modulus can be found for compound A.4, when using silane type II and accelerator type II. This improvement on silica dispersion may be attributed to a more active silanization reaction reaching high degrees of silanization and thus, reducing filler-filler interactions. This observation suggests that silane type II along with accelerator type II provides improved filler-rubber interactions and decreases silica flocculation.

Series B

Figure 62 shows the storage moduli change for batches in series B. As documented in previous sections, in series B and C batch A.2 from series A (larger surface area filler particles) is considered as reference due to the highly adverse flocculation results shown by this compound. It is reflected in this figure that some results of Payne effect are in contradiction with previous results such as Mooney viscosity, flocculation kinetics and bound rubber formation among others.

As it was expected, the absence of silane coupling agent in batch *RB.2* affects negatively to the formation of filler-rubber linkages thus, increasing noticeably the value of Payne effect. From the results obtained from batches B.1 and B.2, it is noticed that increased accelerator contents favorably reduces Payne effect till an optimum level is reached (batch B.1) after which the Payne effect starts raising (batch B.2). Furthermore, when comparing batch B.2 with the reference compound, contradictions can be noticed between Payne effect and Mooney viscosity values as well as with flocculation rate constant. This observation suggests that an undesirable pre curing of the compound might happened during mixing due to the presence of free sulfur released from the silane coupling agent. However, batch B.1 showed the minimum Payne effect value, taking this as an evidence of a positive effect of increasing accelerator contents till an optimum level.

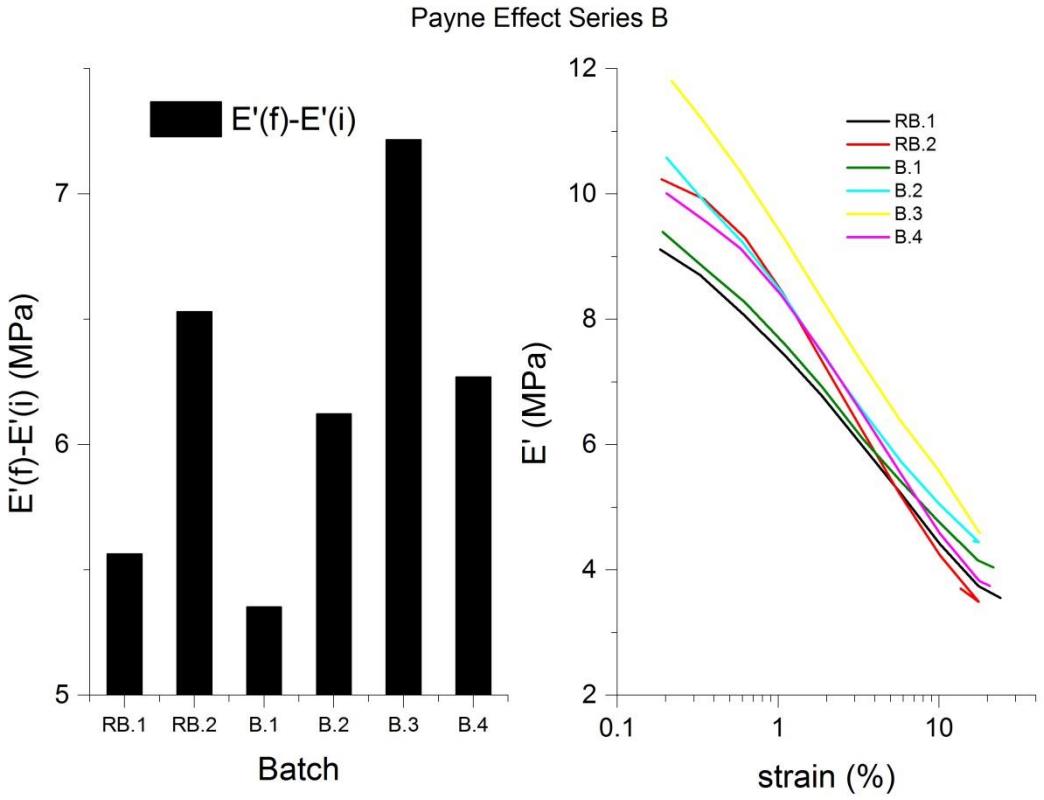

Figure 62. *Payne effect of batches in series B.*

The maximum difference of storage modulus is noticed when the amount of silane coupling agent is increased (batch B.3). This variation leads to a huge increase of filler-filler interactions being in absolute contradiction with previous results as Mooney viscosity, flocculation rate constants and bound rubber formation. This contradiction may be attributed as in previous case to an unexpected pre curing of the compound during mixing. Theoretically, Payne effect should decrease with higher silane coupling agent amounts.

Lastly, it is also noticeable increased Payne effect or filler-filler interactions when masticated rubber is used (batch B.4). According to the results of previous measurements, the use of masticated rubber on rubber compounds does not affect significantly to filler flocculation; however, an increased value of Payne effect can be noticed. The reason might be attributed to the same undesirable pre-curing during mixing due to released free sulfur by silane coupling agents.

Series C

The change in storage moduli with increased/decreased mixing times is depicted in Figure 63. From this figure, the effect of the variations made to the mixing times on filler-filler interactions can be observed. As expected, decreased mixing times (batch C.1) compared with batch *RC.1* show higher values of Payne effect due to less activation of

the silanization reaction. Lower degree of silanization results in increased formation of filler aggregates and thus, in higher values of Payne effect.

Conversely, longer mixing times shows decreased values of Payne effect as well as reduced Mooney viscosity according to previous results. This trend was expected since increased shearing action leads to higher degree of masticated rubber improving filler dispersion within the rubber matrix. Additionally, a higher degree of silanization is reached and filler-polymer interactions become stronger.

Therefore, the results reveal that longer mixing times results in higher filler-rubber interactions and thus, improved filler dispersion. Although longer mixing times show improved results of Payne effect, Mooney viscosity and mechanical properties, it is important to consider that excessive mixing times also may reduce the final properties of the rubber compound.

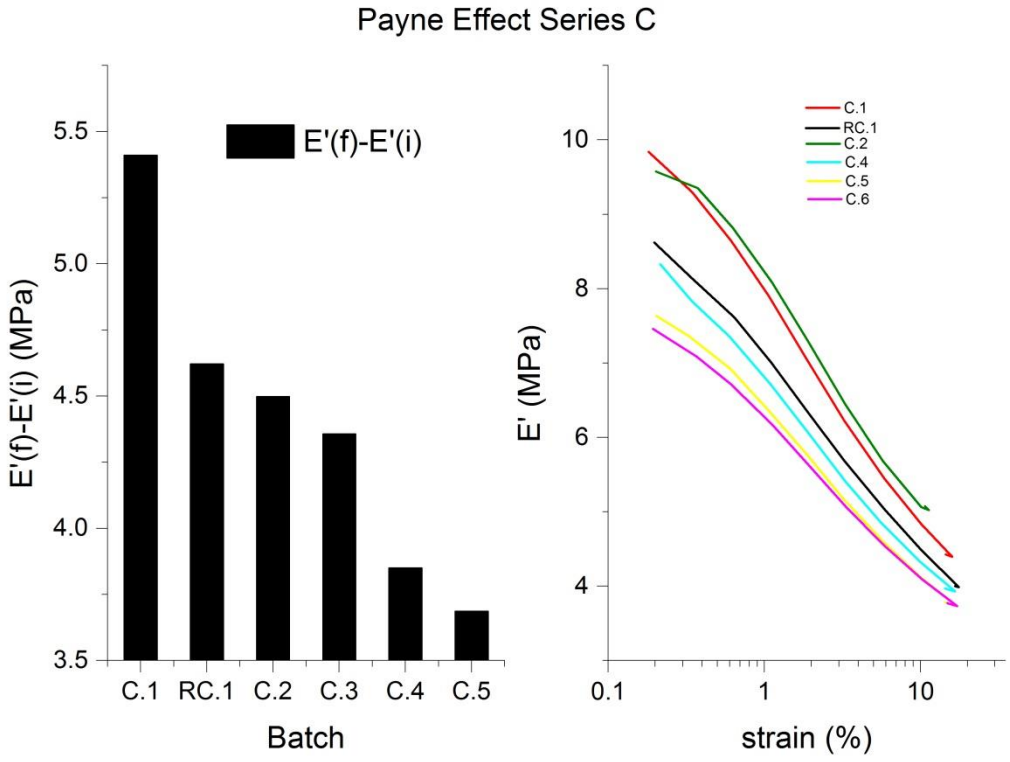

Figure 63. *Payne effect of batches in series C.*

8. CONCLUSIONS

In tyre industry, all the rubber compounds are reinforced with carbon black and/or silica fillers. Rubber reinforcement plays an important role in physical properties of tyres. This thesis was focused on silica filled tyre tread compounds due to its numerous advantages compared with carbon black. In spite of silica presents numerous benefits, its high surface energy and polarity differences with natural rubber lead to the formation of strong filler-filler networks. The formation of agglomerates results in poor filler dispersion in the rubber matrix lowering considerably their reinforcing potential. For that reason, silane coupling agents are added to the recipe in order to reduce the polarity differences and increase the degree of filler-polymer interactions. The reinforcing capacity of silica fillers depends on filler-polymer interactions occurring within the rubber matrix. Increased filler-polymer interactions result in good filler dispersion and favorable physical properties of rubber compounds.

In this study, different measuring techniques were used to assess filler-polymer interactions occurring within rubber matrix, including conventional methods, bound rubber test, tensile test, flocculation studies, and Payne effect. The effects of compound composition and mixing time on filler-polymer interactions were also studied. This thesis starts with a theoretical review in which the main elements of tyre technology are presented. Following chapters presents the measuring techniques used to assess filler-polymer interactions and the results arising from those tests. Based on the results some conclusions can be drawn.

In this thesis three mixing series were prepared with differences in compositions and mixing extension. When analyzing the results obtained from series A several observations were made. Firstly, the effect of silane coupling agent on filler-polymer interactions present a clear trend. From all the measurements performed, the absence of coupling agent results in increased filler-filler formation lowering the reinforcing potential of silica. The adverse effect of large surface area silica (batch A.2) can be seen on the results. Large surface area silica results in strong physical and chemical interaction between the filler and the polymer, however, due to its active surface it also presents stronger interparticle forces leading to the formation of agglomerates during mixing and storage. The filler dispersion is notably reduced affecting negatively to the physical properties of the products. In order to search for better filler-polymer interactions, series B and C considered batch A.2 as their reference compound and variations to its recipe or mixing time were made.

The results showed that when DPG accelerator is added along with the curatives (batch A.5) filler flocculation is notably reduced. All the results obtained for this batch showed improvements when compared to the reference compound, including enhanced

reinforcing index, flocculation rate constant, Payne effect, abrasion resistance, rolling resistance and increased bound rubber content. In addition, this batch shows the optimum curing curve without flocculation and reversion. This favorable behavior is attributed to a more efficient silanization reaction leading to improved material properties. The addition of DPG along with the curatives avoids its adsorption onto silica surface during mixing thus, providing higher degrees of silanization.

The effect of functionalized butadiene rubber (batch A.1) on filler-polymer interactions is not very appreciable. As observed from the results of Payne effect, reinforcing index, curing curves and flocculation rate constants, filler-filler networks are slightly reduced compared to the reference compound.

When using a different silane type, the results reveals that the accelerator is not functioning properly and silanes became inactive leading to poorer physical properties of the material. Filler flocculation develops faster forming filler aggregates.

Finally in series A, when using accelerator type II along with silane type II the results shows better trend than when using silane type II with DPG accelerator. Accelerator type II seems to activate silane type II in a more proper way resulting in slower flocculation development and lower Payne effect. Moreover, better abrasion resistance and lower rolling resistance is achieved with this batch.

Series B considers batch A.2 with large surface area silica as its reference compound. Several variations to its composition were made to detect how they affect to filler-polymer interactions. The results obtained from series B reveal that increased accelerator contents (batches B.1 & B.2) increase the degrees of silanization, thus lowering the formation of agglomerates. Flocculation studies show slower flocculation development leading to improved reinforcing potential of silica.

The effect of increased silane content on filler-polymer interactions can be observed from batch B.3. The results show favorable effects on filler-polymer interactions since the increased amount of silane increases the silanization rate. Increased ethoxysilyl groups are available to react with silanol groups of silica surface, thus the silanization raction rate is increased till no silanol groups are longer free. Filler dispersion is increased and thus improved material properties are reached. However, values of Payne effect are contradictory with these results. The high value of Payne effect within this batch may be attributed to premature crosslinking during mixing.

Lastly, the results of all performed measurements indicate that the use of masticated rubber in batch B.4 shows no influences on filler-polymer interactions compared to the reference compound.

Finally, in series C the influence of mixing extension on filler-polymer interactions was studied. According to the results, shorter mixing times results in faster flocculation development compared with the reference compound, since the degree of silanization reached is notably decreased and filler particles tend to self-associate. However, the results reveal that flocculation is reduced with extended shearing action. Filler aggregates are broken down and enhanced filler dispersion on the rubber matrix is

reached. The properties of the materials are improved due a to favorable filler dispersion.

This thesis made a general introduction to the field of filler-polymer interactions. Several measuring techniques were successfully used to detect and assess fillers reinforcing capability. Related to the selected measuring techniques some conclusions can be made. Payne effect measurement with DMA is an effective and accurate method to assess filler-polymer interactions at low strain amplitudes. From this test the reduction of storage modulus of silica filled rubber with increasing strain amplitude was monitored giving direct information about the extension of the filler-filler networks in the rubber matrix.

The study of the flocculation kinetics of silica also supposes an interesting method to evaluate filler dispersion. The flocculation rate constant of silica gives an idea of how fast the flocculation develops within the rubber matrix. In addition, evaluation of the initial increment in torque on the cure curves of each component provides information about the extension of filler flocculation.

It can be concluded that bound rubber measurement is not a very accurate method to asses filler-polymer interactions since differences in the results can be found between each different repeated measurement. Nevertheless, it is a good method to have an approximated idea of the degree of filler-rubber interactions.

Tensile test is a well contrasted and efficient technique to evaluate filler-polymer interactions since the values of tensile properties such as elongation at break, stress at break and reinforcing index depends on the filler dispersion within the rubber matrix. The better the filler dispersion, the more favorable the tensile properties of the compounds.

The conventional methods used within this thesis are regularly done in rubber industry to measure the properties of every compound. Nonetheless, some useful information related to filler-polmer interactions can be obtained from these measurements as presented in previous chapters.

As a final conclusion regarding the techniques used to measure filler-polymer interactions, it is important to highlight that flocculation studies and Payne effect studies are the right methods to study filler dispersion on the rubber matrix. These methods are very efficient and provide precise information about these filler-filler interactions since they work with a large piece of the sample, differing from other measuring techniques that use a minor piece of the sample providing information of a particular area instead of global information. Moreover, other measuring techniques are tedious and time-consuming, providing not accurate results.

In order to go deeper inside this wide area, further studies may be required. Nowadays, many others measuring techniques are available to characterize the magnitude of filler-rubber linkages intended to understand the importance of reinforcement in rubber industry.

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APPENDIX 1: TEST RESULTS FOR SERIES A

	Series A						
Vulcanization prop.	**RA.1**	**RA.2**	**A.1**	**A.2**	**A.3**	**A.4**	**A.5**
t10 (s)	8.3	4.5	8.4	3.6	3.6	6.4	5.3
t90 (s)	18.6	11.7	19.5	13.7	6.6	15.4	8.2
F_{min} (dNm)	1.1	1.5	1.1	2.1	1.0	1.1	1.0
F_{max} (dNm)	10.4	10.2	10.4	13.6	9.9	11.1	10.0
Static properties							
ML(1+4)	23.5	29.0	24.1	32.6	23.5	23.4	22.3
Abrasion (mm^3)	130.8	216.5	125.3	90.2	159.7	107.5	159.8
Tensile strength (MPa)	17.47	-	16.71	18.90	15.41	15.75	14.31
Elongation at Break (%)	651.54	-	635.59	838.06	491.18	548.47	540.00
Modulus 100% (MPa)	1.15	-	1.10	1.08	0.97	1.36	1.24
Modulus 300% (MPa)	5.68	-	5.47	4.61	4.33	6.86	5.92
RI	4.94	-	4.97	4.27	4.46	5.04	4.77
Dynamic Prop.							
Tan δ max (°C)	-49	-49	-49	-50	-48	-49	-48
Tan δ at 0°C	0.165	0.192	0.167	0.187	0.175	0.163	0.197
Tan δ at 60°C	0.068	0.086	0.063	0.111	0.053	0.057	0.048
E* at 60°C (MPa)	3.1	2.8	2.9	5.0	2.6	3.3	2.8
E" at 0°C (MPa)	0.89	0.91	0.79	1.74	0.71	0.83	0.96
S* 0.20 (dNm)	3.9	4.7	3.8	7.2	3.9	4.1	3.7
Tan δ 0.20	0.099	0.127	0.099	0.168	0.079	0.085	0.082

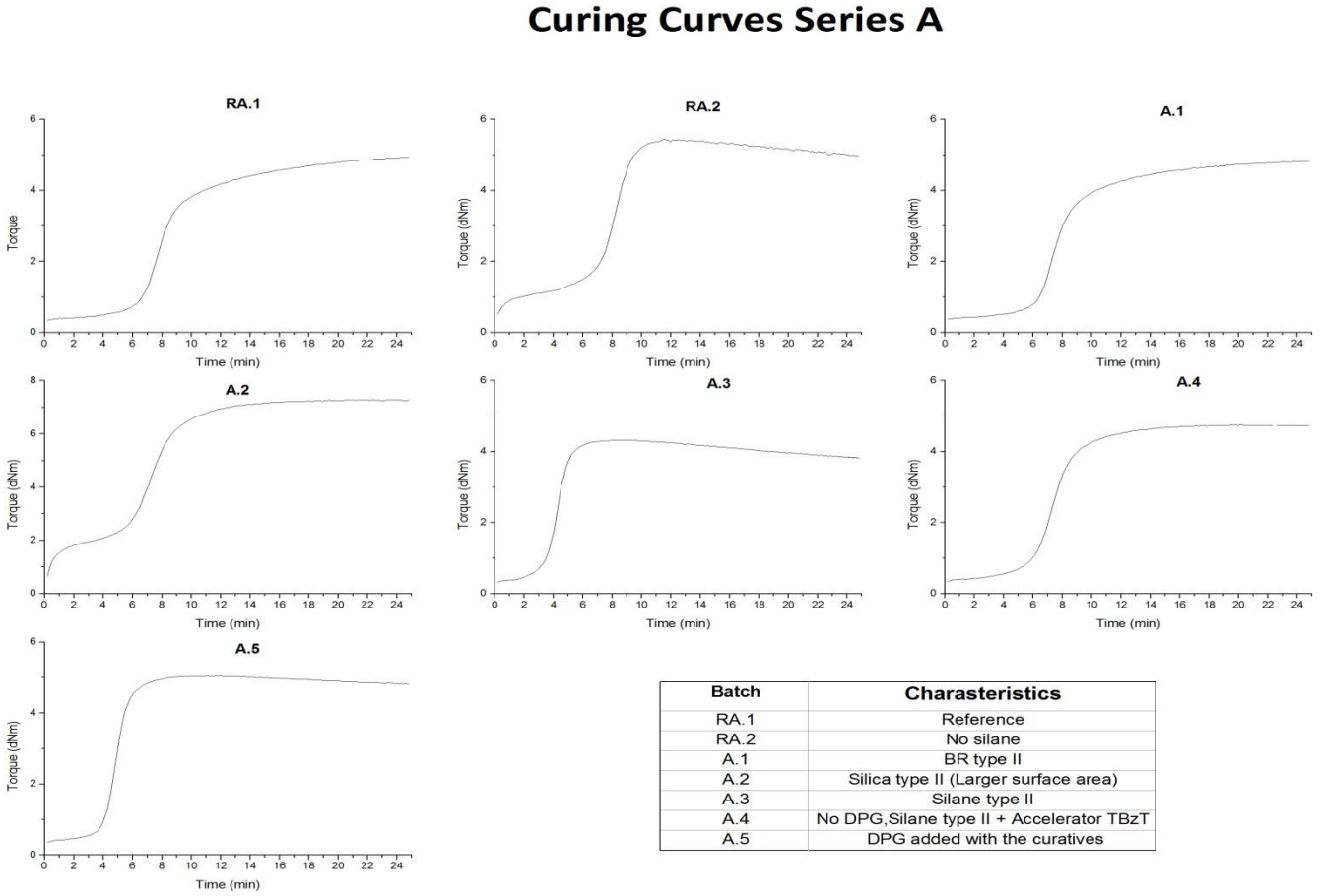
APPENDIX 2: TEST RESULTS FOR SERIES B

	Series B					
Vulcanization prop.	**RB.1**	**RB.2**	**B.1**	**B.2**	**B.3**	**B.4**
t10 (s)	2.7	3.8	3.9	3.1	4.8	2.9
t90 (s)	13.1	15.0	12.7	10.3	18.5	13.5
F_{min} (dNm)	1.5	5.6	1.3	1.2	1.3	1.5
F_{max} (dNm)	14.8	14.5	15.5	15.2	17.1	14.2
Static properties						
ML(1+4)	29.1	70.5	27.4	25.1	25.9	28.8
Abrasion (mm^3)	90.4	-	-	85.5	65.8	94.4
Tensile strength (MPa)	18.46	11.21	17.75	17.65	18.31	17.68
Elongation at Break (%)	530.65	638.85	680.54	576.52	653.52	474.82
Modulus 100% (MPa)	1.37	0.67	1.32	1.58	1.48	1.88
Modulus 300% (MPa)	4.71	2.39	5.84	7.49	6.50	9.58
RI	3.43	3.56	4.42	4.74	4.39	5.09
Dynamic Prop.						
Tan δ max (°C)	-49	-	-48	-47	-47	-48
Tan δ at 0°C	0.178	-	0.177	0.177	0.176	0.181
Tan δ at 60°C	0.091	-	0.091	0.093	0.089	0.095
E* at 60°C (MPa)	6.2	-	7.3	7.4	7.9	7.1
E" at 0°C (MPa)	1.96	-	2.26	2.35	2.45	2.27
S* 0.20 (dNm)	7.6	13.0	7.5	7.6	7.5	7.0
Tan δ 0.20	0.141	0.267	0.128	0.130	0.118	0.138

APPENDIX 3: TEST RESULTS FOR SERIES C

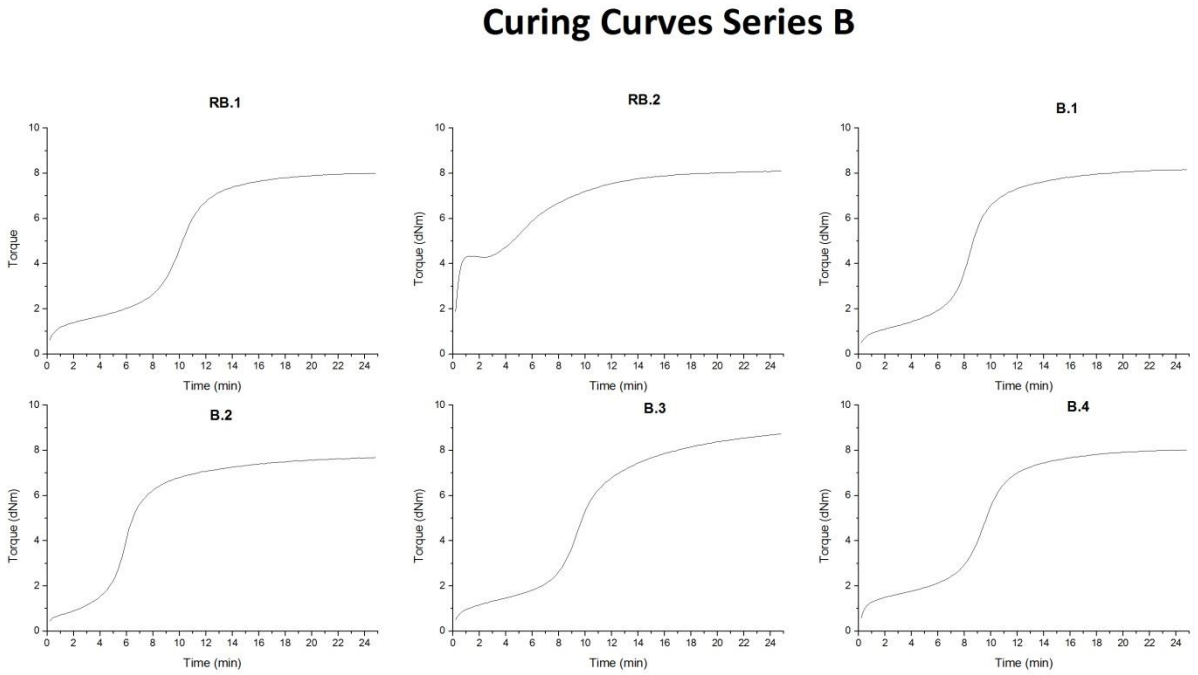
	Series C					
Vulcanization prop.	**C.1**	**RC.1**	**C.2**	**C.3**	**C.4**	**C.5**
t10 (s)	2.1	2.4	3.0	3.5	3.7	4.2
t90 (s)	13.3	13.4	14.2	14.3	14.1	14.4
F_{min} (dNm)	1.5	1.4	1.4	1.3	1.3	1.2
F_{max} (dNm)	14.4	14.7	14.4	13.8	13.5	13.5
Static properties						
ML(1+4)	30.8	28.4	28.4	26.3	25.2	25.4
Abrasion (mm^3)	99.8	71.1	87.2	86.1	79.8	91.8
Tensile strength (MPa)	17.97	18.13	17.96	17.42	17.07	17.41
Elongation at Break (%)	708.04	698.05	676.37	667.93	538.15	483.76
Modulus 100% (MPa)	1.25	1.29	1.28	1.25	1.52	1.75
Modulus 300% (MPa)	5.40	5.62	5.81	5.68	7.68	9.07
RI	4.32	4.35	4.54	4.54	5.05	5.18
Dynamic Prop.						
Tan δ max (°C)	-48	-48	-48	-47	-47	-47
Tan δ at 0°C	0.185	0.185	0.184	0.187	0.185	0.184
Tan δ at 60°C	0.098	0.095	0.095	0.087	0.091	0.094
E* at 60°C (MPa)	6.0	6.2	6.0	5.2	5.2	5.6
E" at 0°C (MPa)	2.01	2.06	1.98	1.71	1.70	1.85
S* 0.20 (dNm)	7.5	7.5	7.1	6.8	6.3	6.3
Tan δ 0.20	0.151	0.149	0.147	0.145	0.144	0.139

APPENDIX 4: CURING CURVES OF BATCHES IN SERIES A



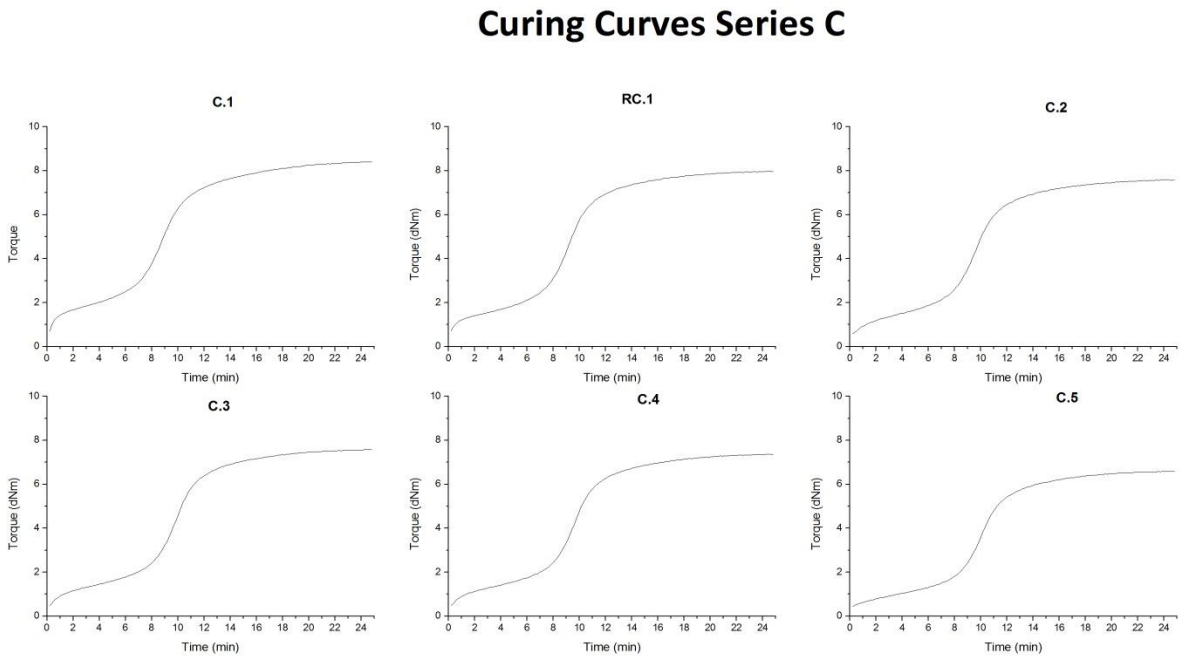
Batch	Charasteristics
RA.1	Reference
RA.2	No silane
A.1	BR type II
A.2	Silica type II (Larger surface area)
A.3	Silane type II
A.4	No DPG,Silane type II + Accelerator TBzT
A.5	DPG added with the curatives

APPENDIX 5: CURING CURVES OF BATCHES IN SERIES B



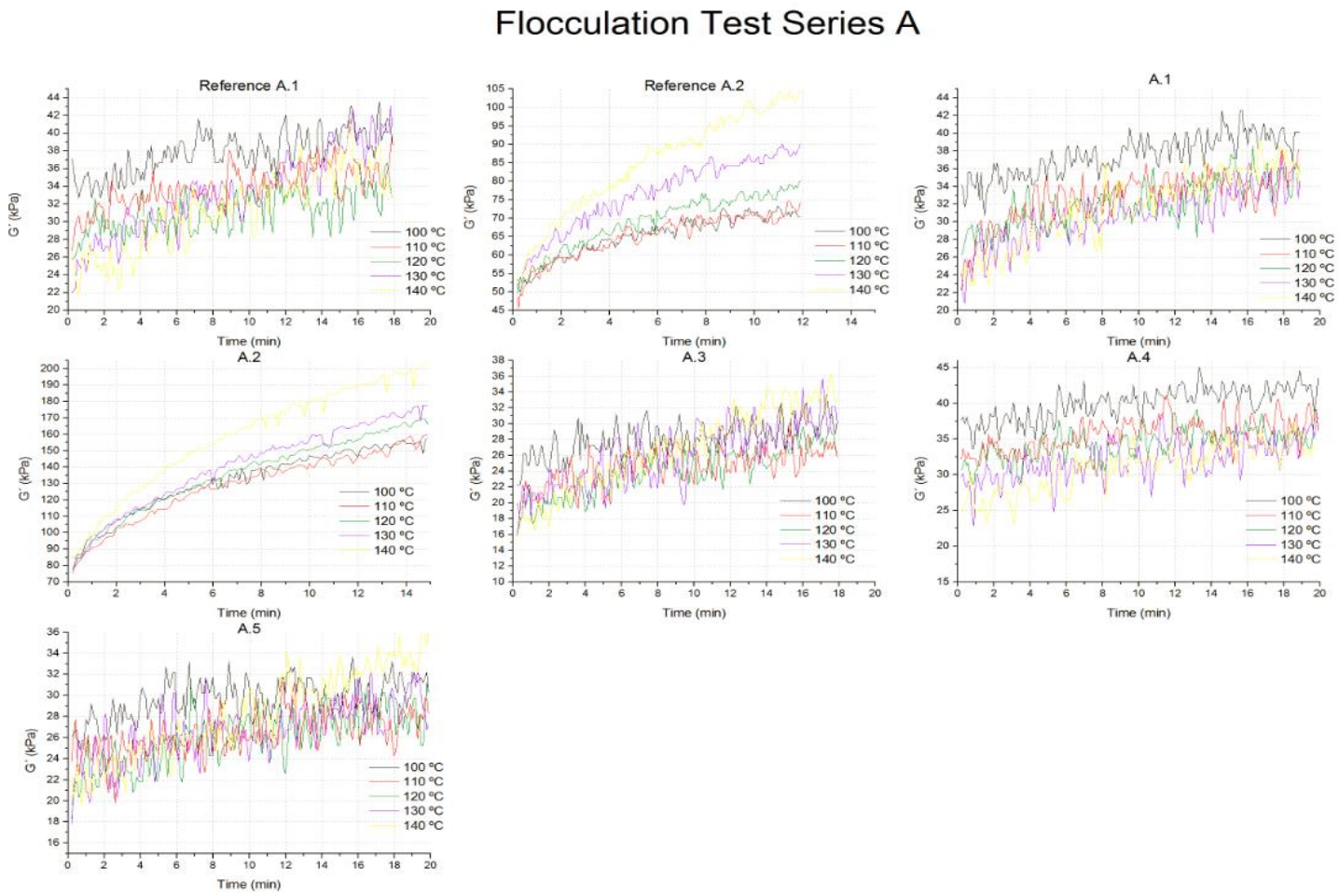
Batch	Charasteristics
RB.1	Reference (batch A.2)
RB.2	Reference without silane
B.1	Increasing DPG up to 2 phr
B.2	Increasing DPG up to 3 phr
B.3	Increasing silane coupling agent
B.4	Masticated rubber

APPENDIX 6: CURING CURVES OF BATCHES IN SERIES C

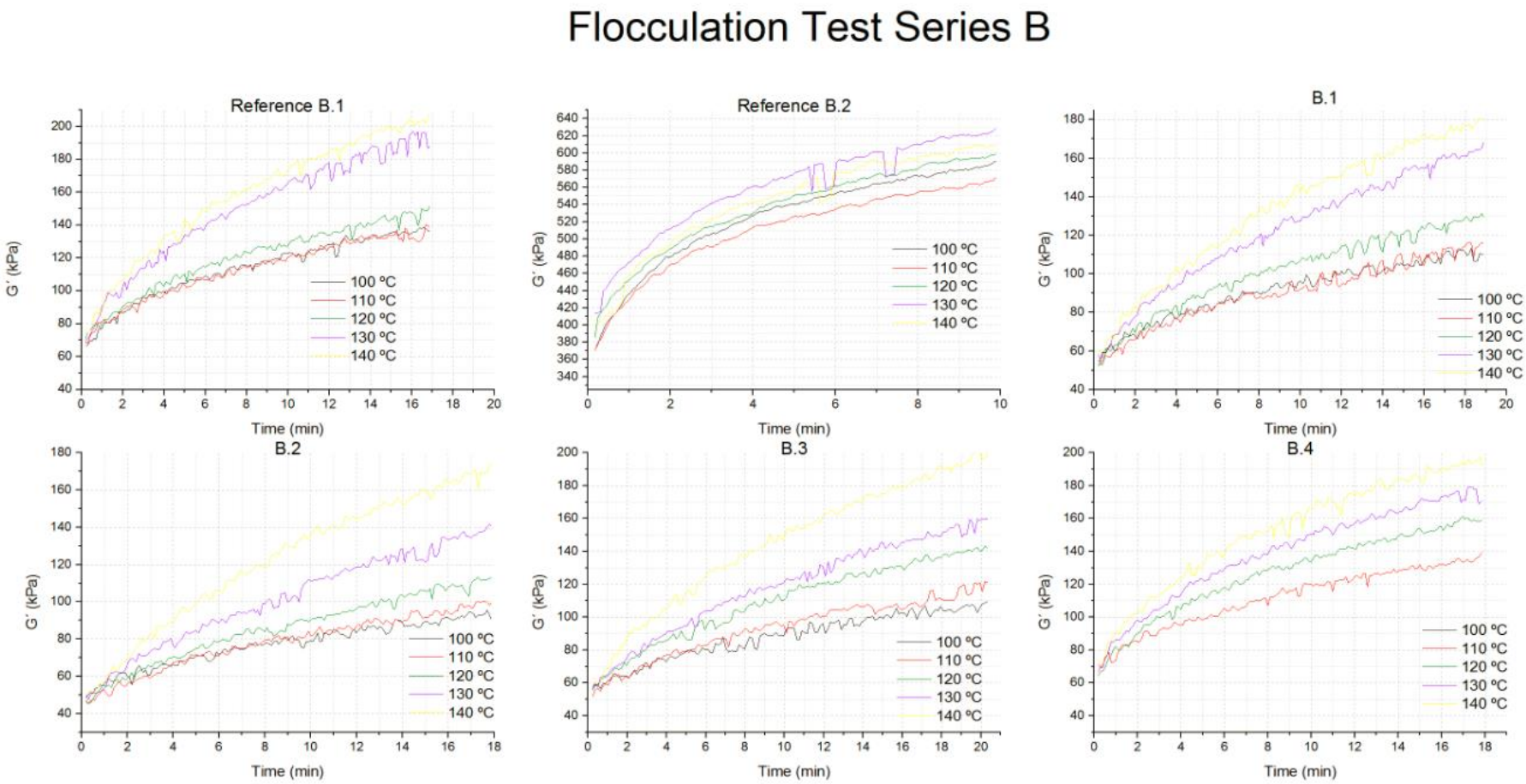


Batch	Charasteristics
C.1	Mixing 40 sec
RC.1	Reference --> Normal mixing (60 sec)
C.2	Mixing 80 sec
C.3	Mixing 100 sec
C.4	Mixing 120 sec
C.5	Mixing 140 sec

APPENDIX 7: FLOCCULATION CURVES OF BATCHES IN SERIES A



APPENDIX 8: FLOCCULATION CURVES OF BATCHES IN SERIES B



APPENDIX 9: FLOCCULATION CURVES OF BATCHES IN SERIES C